Arizona Department of Environmental Quality

Phoenix, Arizona

Arizona Hazardous Air Pollution Research Program Final Report Volume 1: Approach

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1.0 INTRODUCTION AND EXECUTIVE SUMMARY

The Arizona Department of Environmental Quality (ADEQ) and the Arizona Department of Health Services have undertaken a hazardous air pollution research program to evaluate risk to public health in Arizona related to hazardous air pollution and to provide options and recommendations for programs to control the release of hazardous substances into the ambient (outdoor) air. ENSR Consulting and Engineering has been retained to carry out much of the research in coordination with ADEQ.

This report volume is the first presentation of the hazardous air pollution research program's activities. It presents the methods that are being used to carry out the research and describes the progress that has been made to date. Because the findings of the research are currently incomplete and are evolving as analyses continue, this report does not contain any of the research results. They will be contained in a second report volume that will be completed by November 30, 1995.

1.1 What Are Hazardous Air Pollutants?

Hazardous air pollutants (HAPs) can be defined as substances (gases or particles) in the air that may threaten human health through inhalation or other exposure routes. HAPs can be released into the air from a wide variety of sources. The principal sources are combustion and uses of solvents and other chemicals. Businesses, large and small, can be sources of HAPs emissions, from small dry cleaning establishments to large manufacturing facilities. Furthermore, HAPs can be released from common household products such as cleaning products and paints.

HAPs are released upon the burning of gasoline, diesel fuel, oil, natural gas or wood, whether in engines or for home heating. For example, HAPs are emitted by gasoline- and diesel-fueled cars and trucks, as well as by smaller motorized equipment, including lawn mowers and string trimmers.

Chemicals that can produce HAPs through evaporation or use include fuels, solvents, paints, cleaning agents and pesticides. HAPs in gasoline can be released into the air when vehicles are refueled, and HAPs are released when some paints and cleaning solvents dry. Examples of less obvious sources of HAPs from the use of chemicals include swimming pool and domestic water chlorination.

Soils and rocks can contain naturally occurring, small amounts of some HAPs, and particles in car and truck exhaust that contain HAPs can settle onto roads. Activities that generate dust from these materials, such as mining and street traffic, emit those HAPs into the air.

Exposures of people to HAPs depend on where they live, what HAPs are present in the air in that area, and how long they live there. HAPs enter the body directly through breathing. Additionally, HAPs in particles settle out of the air, and they can enter the body indirectly if they settle onto crops, soils where edible crops are grown or onto water bodies used for recreation or drinking. These indirect exposures depend on where the particles are emitted into the air and where they settle to the ground.

Effects from HAPs on human health can be acute, meaning that a brief exposure of minutes or hours can cause an effect. They can also be chronic, in which case effects occur after many years or a lifetime of exposure. An example of an effect from an acute exposure is dizziness or a rash associated with exposure to a toxic gas while an example of an effect from chronic exposure would be increased likelihood of contracting cancer after prolonged exposure to high concentrations of chemical vapors.

The hazard to human health from exposure to HAPs is estimated by a process called "risk assessment." In risk assessment, information from laboratory tests with humans and animals and from studies of the health of groups of the population is used to estimate what effects might be caused by specific real or hypothetical concentrations of HAPs.

1.2 The Mandate for the Arizona HAPs Research Program

The HAPs research program is in response to Arizona Revised Statutes section 49-426.08, which was enacted on July 10, 1992, and became effective on October 10, 1992. It defines the purpose of the program, identifies the research elements, and establishes its schedule:

A. *In cooperation with the Department of Health Services, the United States Environmental Protection Agency and the National Academy of Sciences, the Department of Environmental Quality shall undertake a comprehensive research program to evaluate the existing risk to public health related to hazardous air pollution and to provide options and recommendations for programs to control the release of hazardous substances into the ambient air. In developing the research program, the department shall prepare a research plan and subject that plan to national peer review. The research program shall be funded by monies from the air quality fund established pursuant to section 49-551 and shall include all of the following:*

1. Identification of hazardous substances that are or may be emitted into the ambient air in this state and that present, through inhalation or other routes of exposure, a threat of adverse health effects whether through ambient concentration, bioaccumulation, deposition or otherwise.

2. Identification and evaluation of methods for conducting ambient air monitoring, measuring emissions and performing related analyses.

3. A statewide survey to determine, through direct measurement and appropriate estimation techniques, concentrations of those hazardous substances in the ambient air and to estimate source contributions to ambient concentrations from permitted, nonpermitted and natural sources as well as background concentrations.

4. A statewide survey to identify permitted and nonpermitted sources of these substances and to gather information necessary to quantify emissions.

5. Identification and evaluation of alternative risk assessment methodologies.

6. Evaluation of alternative methods to perform atmospheric modeling and determine source-receptor relationships.

7. An assessment of residual risk after the implementation of controls during the terms of the research program.

8. An evaluation of estimated actual risk from exposure to those substances in this state.

9. An evaluation of the feasibility of, need for and potential methods for establishing ambient air quality standards or health based guidelines for those substances.

10. A public education program to provide information and increase public awareness of hazardous air pollutants and the research program.

11. Other data that the director deems useful or necessary for the purpose of developing the research program.

B. Not later than September 1, 1995, the department shall publish a report of its findings and recommendations resulting from the research conducted pursuant to this section. The report shall include recommendations as to what changes, if any, are

needed to current law to protect public health and the environment from the effects of exposure to hazardous air pollution and shall consider the cost of achieving such changes and any non-air quality health and environmental impacts and energy requirements that may result from the changes. The director shall submit the report to the governor, the president of the senate and the speaker of the house of representatives and shall submit the report for national peer review. The director shall conduct meetings throughout this state in order to present the report to members of the general public and to receive comments.

1.3 Implementation of the Arizona HAPs Research Program

ADEQ began planning the research program in 1993, when it contracted with ENSR Consulting and Engineering to prepare a general research plan and to develop a list of hazardous air pollutants (HAPs) for consideration by the research program. The plan underwent national peer review before finalization in May 1994 (ENSR, 1994). The list of pollutants to be considered, the Arizona Research HAPs List, was finalized in April 1994.

ADEQ started the first operational activities of the research program in April 1994, when it initiated ambient HAP measurements in Phoenix. The measurement program has since been expanded to include additional sites within the state. The ambient air samples collected by ADEQ are analyzed chemically by the Desert Research Institute (DRI) of the University of Nevada.

In late December 1994, ADEQ awarded a contract to coordinate and conduct major operational portions of the research program. A team of atmospheric research organizations, led by ENSR Consulting and Engineering as prime contractor, was selected for this work. The team includes Radian Corporation and DRI as subcontractors for specific aspects of the research. This team's responsibilities include overall management and coordination of the research program, leading detailed planning and technical design of the program, carrying out most of the technical activities, assisting ADEQ in developing and implementing a public education program, and working with ADEQ to prepare final reports to the Arizona Legislature. ADEQ has retained responsibility for conducting the ambient HAP measurements in coordination with ENSR.

A report to the Arizona Legislature on September 1, 1995, is mandated by the enabling legislation. This report volume has been prepared to respond to that requirement. It provides a description of the components of the Arizona HAPs research program and describes how the information from these activities is being used to evaluate potential health risks associated with HAPs.

1.4 Scope of HAPs Research Program

The Arizona HAPs research program activities are being carried out to satisfy the following needs, which represent a step-by-step response to the mandate of the statute:

1. Identify HAP substances that might pose risks to individuals in Arizona
2. Estimate and measure concentrations in the ambient air
3. Estimate exposures of segments of the population to those substances
4. Evaluate the risks to health from those exposures
5. Identify the sources of those substances that pose the highest estimated risks
6. Estimate the "residual risk" that will remain after implementation of federally-mandated controls
7. Evaluate approaches to achieving further reductions, if needed
8. Increase public awareness of HAPs and the research program.

Item 1 was addressed in conjunction with the development of the research plan. The other items are within the scope of the main, operational, portion of the research program.

The list of needs above is quite extensive. Because the research program is the first comprehensive study of HAPs in Arizona, it was necessary to focus the resources of the research program more narrowly in order to obtain meaningful results within a reasonable time frame and budget.

As a first step, in response to the first need above, a Research HAPs List of 676 substances and substance classes was developed from a list of over 1000 substances that may be associated with human activities. Substances were selected for the Research HAPs List based on their potential for posing an adverse effect on human health, whether or not they are actually used or expected to be present in Arizona. This Research HAPs List, which was developed during the planning phase of the research program, served as a starting point for the other facets of the program.

One of the next steps in the research program was to identify those HAPs most likely to be in the ambient air in Arizona, by making ambient air measurements and estimating emissions. On this basis, the risks from a much smaller number of HAPs, representing those chemicals of greatest potential concern, are being analyzed in this research.

The program focuses on analyzing four geographic regions that were selected to represent a large fraction of the state's population and that are characteristic of many of the types of communities in the state:

- The Phoenix area, which includes almost 60 percent of the state's population
- The Tucson area, the second largest metropolitan area in the state, containing about 16 percent of the state's population
- Casa Grande, a low-desert community with a variety of sources, including agriculture
- Payson, a high-elevation community, with a variety of sources including residential wood burning.

(The criteria used for this selection are addressed in some detail in the minutes of the planning workshop for the research operational program, which appear as Appendix A to this report.)

The Tucson and Phoenix areas were selected because they are population centers and also have the HAPs emissions associated with that population. A preliminary screening early in the research program suggested that these two areas would have the state's highest population-weighted indications of health risks due to HAPs, based on their emissions and the toxicities of the emitted species.

Casa Grande was selected to characterize HAPs conditions in a community with a variety of sources, including agriculture. Reliable emission estimates did not exist for many agricultural activities, and thus measurements being made in this region are intended to provide information on the HAPs of importance in an agricultural area. (Yuma was also considered for this purpose, but the potential influence of both Mexican and California emissions would add to the uncertainty in the analysis of conditions there.)

Finally, Payson represents a community under more Alpine conditions, with wood burning emissions and other activities that are typical in such locations. It was chosen instead of

other candidate sites because of availability of data associated with the PM_{10} State Implementation Plan developed by ADEQ in 1995.

In addition to these four regions, a fifth region, that of Nogales, is being addressed in a separate program that focuses on this transboundary area, and thus will not be discussed here. Also, a study in Douglas, another border community, is in its early stages.

The primary focus of the analyses for these locations is on risks due to inhalation of HAPs, because that pathway is expected to be the dominant avenue of risk. To verify this assumption and to quantify effects occurring via other pathways, for the Phoenix region we are assessing the risks due to ingestion of HAPs deposited and absorbed on soil, surface water, and vegetation and in the meat of animals that eat or drink these media.

This research does not specifically address health risks in smelter communities. A separate epidemiological study is being conducted by the Arizona Department of Health Services and the University of Pittsburgh regarding exposure to smelter emissions as a risk factor for development of lung cancer in the Gila Basin (Humble, 1995). This does not mean that copper industry effects are being ignored in the research program, however, because the contributions of copper smelter and mining emissions to HAPs concentrations in ambient air will be determined from the measurement data, using trace elements that are unique markers of those emissions.

It is also important to recognize that the charter of this research only addresses HAPs in the outdoor, ambient air. It does not address HAPs inside homes and buildings, nor does it address HAPs in the work place. Rather, the research is limited to the outdoor air that is generally accessible to the general public.

1.5 Overview of HAPS Research Approach

In broad summary, the HAPs research program for each of the four study regions (Phoenix, Tucson, Payson, and Casa Grande) involves:

- Measuring HAP concentrations in ambient air
- Measuring background HAP concentrations
- Estimating HAP emissions from man-made sources

- Estimating short- and long-term atmospheric HAP concentrations by applying atmospheric modeling and analyzing the HAP measurements

- Evaluating existing health risks from exposure to HAPs through inhalation

- Estimating the residual risk that might remain after implementation of emission controls mandated by the 1990 Clean Air Act Amendments.

Risks in the Phoenix region from indirect exposure to HAPs through pathways other than inhalation are also being evaluated, recommendations are being evaluated for future approaches to management of HAPs emissions, and ENSR is supporting ADEQ with a public education program concerning HAPS.

These tasks are outlined in Figure 1-1. The major elements of these tasks are described briefly below; succeeding sections of this report present the approaches to these tasks in greater detail.

This approach to the HAPs research program generally follows the approach that was presented in the research plan (ENSR, 1994). That approach was reviewed and refined in a two-day workshop held in Phoenix on February 1-2, 1995, which resulted in the research program operational plan (ENSR, 1995). Participants in that workshop included representatives from ADEQ, the Arizona Department of Health Services, Maricopa County, the University of Arizona, and all three organizations in the contractor team (ENSR, DRI and Radian). A list of workshop attendees and the minutes of the workshop are provided in Appendix A.

Referring to the list of research program needs at the beginning of Section 1.4, we noted that meeting the first need, that of identifying substances of possible concern, was begun by the development of the Research HAPs List and is being completed by measuring concentrations in the air and estimating emissions to identify the substances that might pose the greatest risks.

The exposure of the population to those HAPs of greatest potential concern in each study region is being evaluated by two methods: measuring the concentrations of HAPs at certain locations and times, and by predicting HAPs concentrations using an air quality simulation model.

The latter, modeling approach is carried out using an atmospheric model that uses information about emissions sources and weather data for the region to predict how emitted

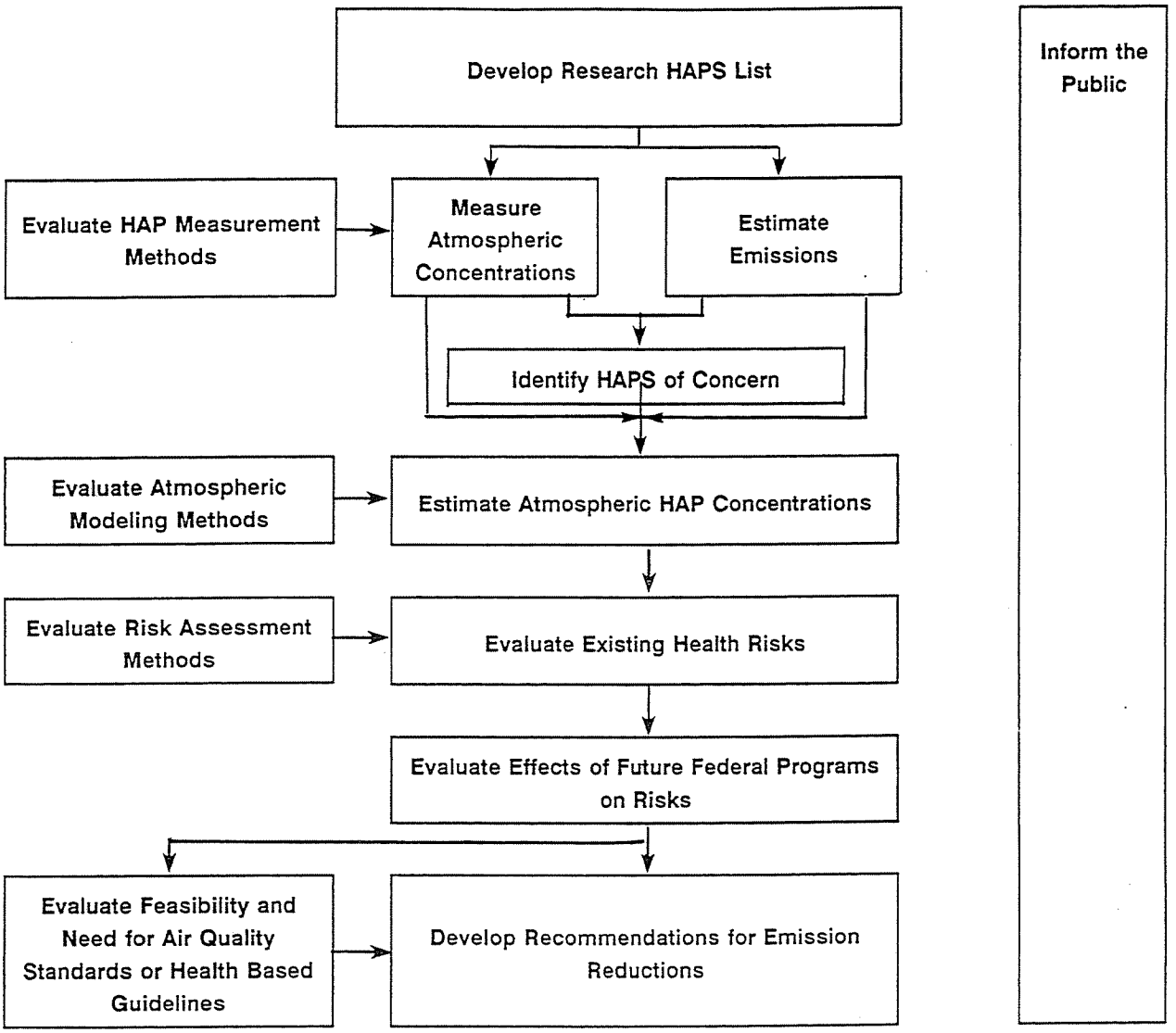


Figure 1-1 Hazardous Air Pollution Research Program Tasks

HAPs will travel in the atmosphere and what the resulting air concentrations will be in various areas within a region. In order to use this technique, a detailed inventory of emissions from all known sources of HAPs in these four regions is being developed. Available measurements of HAPs concentrations are used to evaluate how well the model predicts actual concentrations.

The air concentrations (measured and modeled) are used to evaluate risks to the health of people. Because people come in many sizes and their activity level varies, two general types of people were selected as representative examples of the general population. A "reasonable maximal exposure receptor" was designed to represent people who may have high exposures to HAPs. A "central tendency case receptor" was designed to represent people who may have what are considered to be average exposures to HAPs.

The term "receptor" is used here to stress that these types describe hypothetical people. They are not meant to depict actual or specific individuals in the populations of any of these regions. However, care was taken to select realistic attributes for each of these receptors such that they would be representative of the general population. The results of the high and average exposure cases provide a realistic range of exposure to HAPs and, consequently, a range of human health risks associated with those exposures.

Inhalation exposures to all types of HAPs are being evaluated for each of the four regions in the research program. Although most HAPs are gases, some HAPs are particles. These particles can settle out of the air, possibly onto soil and surface water, depending on where this settling takes place, and thereby contribute HAPs to these media. Exposure to these HAPs might then occur by pathways other than inhalation, for example, by skin contact with soil or by ingestion of fruits and vegetables grown in the soils. To address these routes of exposure, a multipathway evaluation of exposure to HAPs, i.e., an evaluation of exposures by pathways other than inhalation, is being conducted for the Phoenix study region.

Given estimates of exposures, the potential for adverse health effects to occur as a result of those exposures can be estimated. According to the Arizona environmental statutes, an adverse effect to human health is one that results in or significantly contributes to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness, including adverse effects that are known to be or may be reasonably anticipated to be caused by substances that are acutely toxic, chronically toxic, carcinogenic, mutagenic, teratogenic, neurotoxic, or causative of reproductive dysfunction.

The U.S. EPA provides the most comprehensive database of numerical estimates of toxicity. The EPA defines three broad classes of adverse effects: acute effects, or those that result

from short-term exposures; carcinogenic effects, or those that result in the induction of tumors; and chronic noncancer effects, including teratogenic, neurotoxic, reproductive, and other health effects.

The evaluation of most noncancer effects is being based on the common practice of assuming a threshold (a reference dose or reference concentration) for toxic action of a substance. For most carcinogenic compounds, however, no threshold is assumed, so that any level of exposure, no matter how small, carries with it a finite probability of evoking an adverse effect. That probability, determined from values provided by the EPA, represents an upper bound estimate of the risk of contracting cancer as a result of the evaluated exposure. "Upper bound" means that the true risk, which cannot be precisely defined, is not likely to be higher, but may be lower (and may be close to zero in some cases). At the same time, it should be recognized that the effects from exposure to multiple HAPs are not well understood and may actually increase true risk. Cancer risk estimates are generally presented in terms of probability, such as a one in one million or one in ten thousand chance of contracting cancer as a result of the exposure evaluated.

Two risk evaluations are being made for each region. Health risks are being evaluated for HAPs under conditions of exposure based on current estimates of emissions and the current ambient monitoring data, and also under conditions that may exist after full implementation of emission controls mandated by the 1990 Clean Air Act Amendments. For the latter case, "post-control" emissions estimates are used to predict "residual" exposures and risks.

All of the activities of the research program are described in greater detail in the subsequent sections of this report, and further detail on some aspects is provided in the appendices.

1.6 Current Status of Research Program

The research efforts began with the preparation of the HAPs research plan. Several technology evaluations were made during the course of preparing the HAPs research plan. The techniques evaluated included those for measuring HAPs in ambient air and in source emissions, for performing atmospheric modeling and determining source receptor relationships, and for performing risk assessments. Recommendations were made, and those evaluations and recommendations provided guidance for the approach that has been followed during the research program. These method evaluations fulfilled items 2, 5, and 6 of the objectives list in the enabling legislation, as presented in Section 1.2.

Also, as the research plan was completed, a Research HAPs List was prepared to respond to item 1 in the enabling legislation.

ADEQ began monitoring of HAPs in ambient air in Phoenix in April 1994 and has subsequently expanded its monitoring efforts to other locations in each of the four selected study regions and has also performed measurements to characterize HAPs emissions from some area sources. This monitoring, which addresses item 2 in the enabling legislation, is ongoing.

In order to test the risk assessment approach that was selected, the processes of emission inventory development, atmospheric modeling, and risk assessment were exercised for selected chemical species in Phoenix. Evaluation of the results of this exercise and comparison of model predictions with measured concentrations showed that the approach provided good results in some cases but had shortcomings in others. In particular, this initial exercise identified some gaps and limitations in the initial emissions inventory and also suggested some improvements for other aspects of the approach. Additions and improvements to the inventory and to other components are now being finalized. Then, the process will be repeated in Phoenix and implemented in the other regions to provide the risk evaluations that are a goal of this research. These steps respond to items 3, 4, and 8 of the enabling legislation.

Some other tasks will also address these items. In Phoenix, health risks due to pathways other than inhalation will be evaluated. The contributions due to smelter and mining emissions will be inferred by receptor modeling techniques.

Emission controls that have to be implemented under the provisions of the Clean Air Act are being identified and an emissions inventory that reflects the imposition of these controls is being developed. Using that inventory, the risk assessment process will be repeated to estimate the residual risk after control and to identify the need, if any, for future emission control strategies. These analyses address item 7 of the enabling legislation.

An evaluation of the need for establishing ambient air quality standards or health-based guidelines (item 9 in the enabling legislation) will be carried out after the residual risk assessments are completed. Alternative approaches to such standards were evaluated in the research plan.

Finally, in response to the public education mandate (item 10 of the enabling legislation), a public information leaflet about the HAPs research program has been prepared and distributed. A copy is included at the end of this section. Recommendations will be developed for educating the public about the research program's findings, and additional materials will be prepared to disseminate and interpret the research results when the final report is released.

Arizona Hazardous Air Pollution Research Program

1. What is the Hazardous Air Pollution (HAP) Research Program?

The Arizona Department of Environmental Quality (ADEQ) and the Arizona Department of Health Services are undertaking this research program to evaluate existing risk to public health in Arizona related to hazardous air pollution and to provide options and recommendations for programs to control the release of hazardous substances into the ambient (outdoor) air.

The program has been developed in response to Arizona Revised Statutes Section 49-426.08. The program will address the following:

- Identification of hazardous substances emitted into the ambient air.
- Air monitoring and air modeling at four selected regions in Arizona to estimate ambient concentrations of hazardous substances.
- Determination, through risk assessments, of the estimated actual risk from exposure to these substances in Arizona.

2. What are hazardous air pollutants (HAPs) and how are people exposed?

Hazardous air pollutants are substances that may threaten human health through inhalation or other exposure routes. These pollutants can be released into the air by a variety of sources, such as vehicle emissions, residential activities and consumer products, agricultural activities, wood-burning stoves, and natural background. Over 500 HAPs have been identified for investigation in this study.

People are most likely to be exposed to HAPs by inhalation (breathing both indoor and outdoor air). These chemicals can also settle out of the air onto soil and water surfaces and crops.

3. What health effects can HAPs cause in people?

Not everyone who is exposed to HAPs will develop health effects. The health effects are dependent on how large a dose a person receives and for how long. The most obvious health effects are respiratory problems, such as bronchitis and asthma. Exposure to HAPs can also cause damage to the liver and nervous system and in some cases cancer.

4. Where are the four study regions and how were they selected?

The four regions chosen by ADEQ are Casa Grande, Payson, Phoenix and Tucson. Each region is representative of the state's various population and geographic areas. Phoenix and Tucson are representative of the large metropolitan areas and are where the majority of Arizona citizens live. Casa Grande is representative of a low desert agricultural area and Payson is characteristic of a forested rural community.

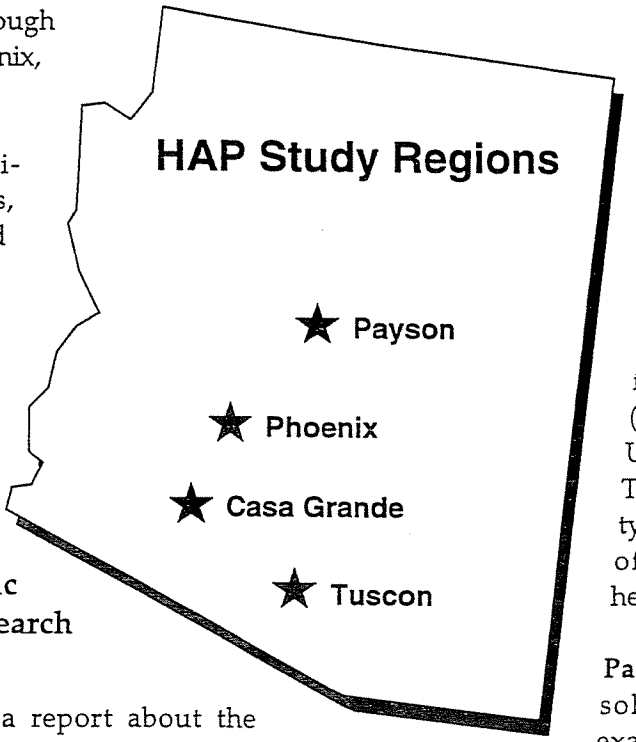
5. How are air HAPs samples taken?

The air monitoring is done by collecting samples of the HAPs over a 24-hour period in a region. There are two types of HAPs to be collected: particulate matter and gases. These samples are collected on filters, chemically treated foam, and in stainless steel containers. Once collected, the samples are sent to a special laboratory for analysis.

6. What will be done with the air monitoring results?

The air monitoring results will be used along with an inventory of emissions, air modeling, health effects, and demographic information to do a risk assessment for each region. The risk assessment will estimate exposures and resulting health risks due to HAPs through inhalation and, in Phoenix, contact with soil.

ADEQ will also estimate HAPs emissions, air concentrations, and resulting health risks that would occur after full implementation of emission controls mandated by the 1990 Federal Clean Air Act Amendments.



7. How will the public learn about the research program's results?

ADEQ will prepare a report about the research's results and will present this report to the Arizona Legislature and the public in the Fall of 1995.

Glossary

Hazardous Air Pollutant: Air pollutant that may pose a potential health risk when emitted into the air.

Risk Assessment: A study process involving identification of toxic substances in the air, evaluation of conditions under which a population group could have been exposed, analysis of the toxicity of the specific substances and calculation of increased risks of adverse health effects related to the exposure.

Risk: A common definition of risk is the "possibility of suffering harm or loss; danger" (Webster's II; New Riverside University Dictionary, 1988). This definition can apply to any type of risk, including sources of potential risk to human health or the environment.

Particulate Matter: Particles of solid or liquid matter, some examples are particles of soot, dust aerosols, fumes and mists.

Atmospheric Modeling: The dispersion of pollutants in a geographic area and how the meteorology (wind, precipitation, turbulence) disperses the emissions in the atmosphere. Modeling will also estimate how much of the emissions are deposited on the ground, plants, and water.

8. How do I get more information about the program?

To get more information about the program and the research study, call Jim Matthews, ADEQ Public Information Officer, at (602) 207-2300.

2.0 ATMOSPHERIC HAP MEASUREMENTS

The research program includes measurements of atmospheric HAP concentrations for several reasons. When the research program began, it was not known which HAPs on the Research HAPs List are actually present in Arizona's air, so measurements were initiated to identify HAPs that could be detected in the atmosphere. The measured HAP concentrations are also being used as part of the estimation of health risks and are being compared with results of the atmospheric simulation model to evaluate how well the model predicts concentrations. Because the health risks are being estimated for the general population in each of the four study regions, these measurements are being made in residential neighborhoods to characterize concentrations where people live. Additional measurements are being made at a remote location to characterize HAP concentrations that are not directly attributable to emissions in the regions (i.e., "background" values). Finally, atmospheric measurements are providing information on the types of HAPs emitted by some sources by making measurements in the vicinity of those sources.

2.1 Measured Chemical Species

Table 2-1 lists the 83 HAPs that are being measured routinely. Although it would be desirable to measure all of the substances on the Research HAPs List, it was determined during development of the Research Plan that measurement methods do not exist for most of them. Additionally, methods exist for some HAPs that are not shown in the table, but those methods were too costly for routine use within the resources available to the research program. However, a small number of measurements of three additional HAPs (mercury, dibenzo furans and 2,3,7,8-tetrachlorodibenzo-p-dioxin) are being made to provide initial information about their presence in Arizona.

Measurements are also being made of 30 chemical species that are not considered HAPs for use in analysis and interpretation of the research program's results. In particular, the amounts of many non-hazardous chemicals in the atmosphere can be used as "fingerprints" of the emissions from some types of sources to estimate how much those sources contribute to the HAPs. This technique, called receptor modeling, is described further in Section 7.

TABLE 2-1

HAPs Measured in the Atmosphere During the Research Program

acetaldehyde
acetone
acrolein
aluminum compounds[a]
antimony compounds[a]
arsenic compounds[a]
barium compounds[a]
benzaldehyde
benzene
biphenyl
bromine compounds[a]
1,3-butadiene
cadmium compounds[a]
carbon tetrachloride
chlorobenzene
chloroform
total chromium compounds[a]
cobalt compounds[a]
copper compounds[a]
crotonaldehyde
1,2-dibromoethane
o-dichlorobenzene
p-dichlorobenzene
1,2-dichloroethane
cis-1,2,-dichloroethylene
trans-1,2-dichloroethylene
ethylbenzene
formaldehyde
n-hexane
indium compounds[a]
iron compounds[a]
lead compounds[a]
manganese compounds[a]
mercury compounds[a]
methyl chloroform
methyl ethyl ketone
methylbromide
methylene chloride
molybdenum compounds[a]
nickel compounds[a]
n-nonane
perchloroethylene
phosphorus compounds[a]
potassium compounds[a]
propionaldehyde
selenium compounds[a]
silver compounds[a]
strontium compounds[a]
styrene
sulfur compounds[a]
thallium compounds[a]
tin compounds[a]
toluene
1,1,2-trichloroethane
trichloroethylene
2,2,4-trimethylpentane
vinylidene chloride
m/p-xylene
o-xylene
yttrium compounds[a]
zinc compounds[a]

Polycyclic Organic Matter (POM), including:
- acenaphthene
- acenaphthylene
- anthracene
- benz(a)anthracene
- benzo(a)pyrene
- benzo(b)chrysene
- benzo(b+j+k)fluoranthene
- benzo(ghi)perylene
- chrysene
- dibenzo(ah+ac)anthracene
- 2,6+2,7-dimethyl naphthalene
- 1,7+1,3+1,6-dimethyl naphthalene
- 1,8-dimethyl naphthalene
- 2,3+1,4+1,5-dimethyl naphthalene
- 1,2-dimethyl naphthalene
- fluoranthene
- fluorene
- indeno[123-cd]pyrene
- 1-methyl naphthalene
- naphthalene
- phenanthrene
- pyrene

Notes:

[a] The total concentration of the chemical element is measured, regardless of the compounds that contain it

2.2 Residential Neighborhood Measurements

HAPs are being measured for a full year in one residential neighborhood in each of the four study regions. Measurements began in Phoenix in April 1994 and were completed at the end of March 1995. Residential neighborhood measurements began in Payson in January 1995 and will be completed in January 1996. Measurements in Casa Grande and Tucson began in April 1995 and are scheduled to conclude in April 1996. Although it would have been preferable to make measurements in all four regions at the same time, the study regions were not selected until January 1995, when the Department's contractor ENSR was hired. Because of the time required to analyze and interpret results from the measurements, the research program findings to be presented near the end of the year will not be able to include measurements made after August 1995. Measurements made after that date will be analyzed and presented in a subsequent report.

These measurements are made by collecting a set of samples of the air over a 24-hour period beginning at 10:00 am every sixth day and measuring the total amount of each measured species that is in the sample. The methods used are summarized in Section 2.5. The six-day sampling frequency provides a balance between collecting enough samples to characterize annual average concentrations, which are required to estimate health risks from long-term exposures, and available resources, which are not adequate to collect samples every day. The six-day schedule allows measurements to be spread over all of the days of the week during a year, avoiding biases in the results that could be caused by weekly patterns of emissions.

Sampling began in Phoenix, at a location named the "Super Site" because of the abundance of monitoring equipment there (not all for this research program), on April 2, 1994, and ended on March 28, 1995, when a full year of sampling was completed. Data from a total of 59 sample sets are available. The site is in a fenced compound on 17th Avenue, north of Campbell, in a residential neighborhood approximately two kilometers north of the center of Phoenix.

Regular sampling began at Payson at the Weber Well site on January 14, 1995. The site is centrally located in a fenced water well enclosure, approximately 200 meters west of State Route 87, in the main down-wind drainage basin west and south of the center of town. Although this location is not strictly in a residential neighborhood, the data are expected to be characteristic of residential exposures because of Payson's relatively small geographic size.

Residential neighborhood sampling started in Casa Grande on April 15, 1995. The site is collocated with a Pinal County air quality measurement site on the roof of the Department of Economic Security building at 401 Marshall Road. Although the site is located in a commercial district, it is near several residential neighborhoods and less than one kilometer from large active agricultural fields.

Sampling in Tucson began on April 9, 1995, utilizing the sampling equipment that previously operated at the Phoenix Super Site. The site is on the roof of a storage building at Park and Adams Streets on the University of Arizona campus, adjacent to a residential neighborhood.

2.3 Background Measurements

Regional background measurements began at a remote site approximately 80 kilometers north of Phoenix, on November 16, 1994. The site is located in a fenced compound on a mountain top near Hillside. It is a remote site, requiring a four wheel drive vehicle to reach it via a dirt road. Because of the time required to reach the site, a sample is collected once every twelve days, rather than once every six days as at the residential neighborhood sites.

Sampling was also conducted to attempt to characterize background concentrations in the Payson region at the Payson Water Tank Site. The site was located on a hill top northwest of the center of Payson, approximately 0.5 km from the Payson airport, generally upwind of the town. Three sample sets were collected between December 22, 1994, and January 9, 1995, on the basis of meteorological conditions. Sampling was stopped at this site because of high concentrations that were attributed to nearby sources, so that the measurements were not truly characteristic of background concentrations in the Payson area.

2.4 Emission Source Oriented Sampling

Measurements were made in Phoenix to characterize emissions from on-road motor vehicles, at Williams Air Force Base to characterize agricultural emissions, at Payson to characterize wood burning emissions and at a truck stop in Tonopah to characterize emissions from heavy duty diesel vehicles. Measurements have also been made at two locations in Phoenix to evaluate concentrations in residential neighborhoods in the vicinity of industrial areas.

The motor vehicle-oriented sampling took place at the Indian School Road site in Phoenix. The site is in a fenced compound near 33rd Avenue and Indian School Road, approximately 10 meters (33 feet) from traffic on Indian School Road. This is the location of the Maricopa County Environmental Services Department carbon monoxide "hot spot" monitor. Sampling began on June 13, 1994, and continued for 10 sampling days on the six-day schedule to

characterize motor vehicle emissions during the summer. Sampling began again on December 15, 1994, to characterize emissions during use of oxygenated fuels. Sampling during this winter period was scheduled on the basis of meteorological conditions to occur during inversions when maximum concentrations were expected to occur, leading to collection of seven samples by December 28, 1994, when sampling ended at this site.

Sampling to characterize emissions from heavy duty diesel vehicles took place at a truck stop in Tonopah between March 6 and March 31, 1995. This location is approximately 55 kilometers west of Phoenix on Interstate 10. There are no other emission sources in the vicinity, so ambient samples collected there were dominated by emissions from trucks that are idling and entering and leaving the facility. A total of ten 12-hour samples were collected. The sampling media used at the other sites were supplemented with Tenax cartridges to provide supplemental information concerning high molecular weight chemical species and with quartz fiber filters for measurement of particulate carbon.

Preliminary sampling to characterize agricultural activities began at the former Williams Air Force Base, which is closed, on May 20, 1994. The site is approximately 40 kilometers southeast of the center of Phoenix in an agricultural area. Four sample sets were collected on the six-day schedule.

Limited sampling to characterize wood burning emissions began in Payson at the Weber Well site on January 14, 1995. The sampling was conducted on the basis of meteorological forecasts of low temperatures and strong inversions, which would lead to elevated concentrations of emissions from residential wood burning. Three sample sets were collected.

Measurements to characterize concentrations in the vicinity of an industrial area were made at Brooks Water Reservoir in the City of Mesa over two consecutive 24-hour periods beginning on June 27, 1995. The site was in a fenced compound at the end of Brooks Street at a covered water storage facility. HAP emission sources near the site include an electronics plant one kilometer to the west, a sporadically used railroad track 150 meters to the north and a large cabinet manufacturer 150 meters to the southeast.

Additional measurements to characterize concentrations near industrial and other emission sources were made for four consecutive days beginning on July 18, 1995, at a Phoenix police station located at 16th Street south of Mohave Street. Possible HAP emission sources in the vicinity of the site include several large sand and gravel operations one kilometer to the southwest, a railroad terminal one kilometer to the north, two freeways approximately 0.5

kilometers to the east and south, light industrial sources to the west, and Sky Harbor airport two kilometers to the east.

2.5 Atmospheric HAP Measurement Methods

Table 2-2 lists the HAP sampling and analysis methods used for ambient measurements during the research program. The program utilizes four sets of sampling equipment located at fixed sites and one set in a mobile sampling trailer. The mobile sampling trailer was custom-built for ADEQ to facilitate short-term sampling at various locations, such as the Tonopah truck stop and the source oriented sampling in the Phoenix area at Brooks Reservoir in Mesa.

Appendix B provides detailed descriptions of these methods.

TABLE 2-2

HAP Sampling and Analysis Methods

HAP Type	Sampling Substrate	Sampler	Analytical Method
Volatile Organic Compounds (e.g., benzene)	6 liter SUMMA polished stainless steel canister	DRI- and ADEQ-constructed canister samplers	Cryogenic concentration and high resolution capillary column gas chromatography with flame ionization and electron capture detectors
Semi-Volatile Organic Compounds (e.g., benzo(a)pyrene)	Teflon-coated glass fiber filter followed by polyurethane foam (PUF)/XAD-4/PUF cartridge	Graesby-Andersen PS-1 High Volume PUF sampler	Soxhelet extraction with diethyl ether in hexane (PUF) and dichloromethane (filter and XAD-4) followed by gas chromatography/mass spectrometry
Carbonyls (e.g., formaldehyde)	Dinitrophenylhydrazine on C_{18} Sep-Pak cartridge	DRI-constructed carbonyl sampler	Elution with acetonitrile followed by high performance liquid chromatography with UV detection
PM_{10} Chemical Elements (e.g., arsenic)	37 mm diameter Teflon membrane filters	Graesby-Andersen Dichotomous Samplers	X-ray fluorescence

3.0 HAP EMISSION ESTIMATION

Estimates of HAP emissions in each of the four study regions are being used for several purposes. First, they are being used along with the atmospheric HAP measurements, described in the preceding section, to help identify HAPs that may actually be present in the regions, following the approaches described in Section 4. Secondly, they are being used, as described in Section 7, to attribute HAP concentrations in the atmosphere to emission sources. Finally, they are being used as input to the atmospheric simulation modeling described in Section 5 to estimate atmospheric HAP concentrations throughout the study regions.

These uses of the emission estimates require that the emissions information be provided with varying levels of resolution. Identifying the HAPs that might be present in a region requires that estimates be made of total emissions of as many HAPs on the Research HAPs List as possible. Attributing atmospheric concentrations to the various types of emitting sources in a region requires that estimates of total emissions of the HAPs that are of concern from a health risk perspective be available by type of emission source. The atmospheric simulation model requires estimates by geographic location, season and time of day of emissions of the HAPs of concern.

In general, HAPs are emitted to the atmosphere in one of four ways:

- From the combustion of fuels, such as in cars and natural gas utility boilers
- From the evaporation of solvents and paints that contain HAPs, such as methylene chloride from degreasing solvents
- From the release of dust that contains HAPs, such as cadmium from unpaved roads and mining operations
- From certain manufacturing operations, such as arsenic from copper smelting or benzene from petroleum refining

Very few actual measurements of HAP emissions are available. Therefore, various types of techniques need to be applied to estimate HAP emissions. These techniques vary with the type of emission source and with the information that is available about the source.

Initial estimates of emissions have been made for the research program. ADEQ and the research program contractors are reviewing these initial estimates to identify potential inaccuracies that might have the most significant effects on the validity of the research program's findings and are currently collecting additional data to reduce those uncertainties.

The following discussion summarizes the development of the initial emissions estimates. The approaches are presented in detail in Appendix C.

3.1 Facility Emissions

Initial emissions estimates have been developed for over 300 individual facilities, such as electric utility generating stations, electronics manufacturing facilities, and furniture manufacturers. For many of these facilities, HAP emission estimates were obtained from permit files at local air pollution control districts and the ADEQ. In other instances, data were obtained from the United States Environmental Protection Agency's (U.S. EPA) toxic release inventory, which is developed under the federal community right-to-know laws. Under these laws, facilities that use or manufacture toxic chemicals in quantities above specific thresholds must report annual releases of toxic chemicals to land, air, and water. The reported releases to air are used as emission estimates along with data from Arizona agency permits.

HAP emission estimates were not available for all facilities. To supplement the data obtained from permit files and the U.S. EPA, various engineering procedures were used to estimate emissions from many facilities. These estimating techniques use previously developed information to estimate emissions of HAPs to the atmosphere.

For example, HAP emissions from natural gas-fired boilers can be estimated from factors that characterize the amount of a HAP emitted per amount of fuel that is consumed. On average, a small natural gas boiler emits approximately 0.04 pounds of formaldehyde for every million cubic feet of natural gas burned. This factor is termed an *emission factor*. Emission factors have been developed from actual measurements of HAP emissions from various types of operations.

For other operations, previously estimated emissions of total volatile organic compounds (VOC) and particulate matter can be disaggregated into their individual components, some of which are HAPs. For example, gasoline vapors are emitted from bulk storage tanks. Data collected as a part of this research program are being used to determine how much of this gasoline vapor is comprised of benzene, 1,3-butadiene, and other HAPs. This approach is referred to as *speciation*.

3.2 Dispersed Area Sources

Emissions from many small, dispersed sources of HAPs are also estimated. Examples include small facilities, such as chrome platers, neighborhood dry cleaning facilities, and gas stations; and activities such as painting and burning wood for home heating. Individually, these sources are small, but collectively, the emissions from these dispersed area sources can be quite large and are therefore important sources of HAPs. HAP emissions are being estimated for over 100 different types of dispersed area sources.

The emission factor and speciation techniques described in Section 3.1 are also used to estimate emissions from dispersed area sources. For example, the amount of gasoline sold in a region can be obtained through sales tax records and used with an emission factor to estimate the amount of gasoline vapors emitted from the refueling of automobiles. The gasoline vapors are then disaggregated into chemical constituents using speciation data.

3.3 Mobile Sources

Fuel evaporation and tailpipe exhaust gases from mobile sources are also important sources of HAPs. This includes gasoline- and diesel-powered motor vehicles, as well as the following types of sources:

- Lawn and garden equipment (e.g., lawn mowers)
- Construction equipment (e.g., bulldozers)
- Industrial equipment (e.g., forklifts)
- Farm equipment (e.g., tractors)
- Aircraft
- Locomotives
- Boats

For all mobile sources, total VOC emission estimates are first developed, and then the VOC estimates are disaggregated into individual components (i.e., speciated). Special studies were conducted in Phoenix so that region-specific data could be used to speciate the VOC emission estimates from gasoline- and diesel-powered motor vehicles.

3.4 Emission Locations and Changes in Time

As described previously, the atmospheric simulation modeling requires HAP emission estimates by geographic location. HAP emissions from individual facilities are located from facility location information in permit files. For dispersed area sources and mobile sources,

emissions are distributed in the regions according to land use patterns. For example, emissions from lawn and garden equipment are associated with housing. Emissions from motor vehicles are distributed according to the roadway network.

Seasonal and time-of-day variations in the emissions are also important inputs for the atmospheric model. Annual facility emissions are adjusted for seasonal and time-of-day variations using operating schedule data that are obtained from the permit files. For dispersed area sources and nonroad mobile sources, seasonal patterns are based on previous studies. For example, residential wood combustion occurs primarily in the winter, with lesser amounts in the fall and spring, and virtually no wood combustion during the summer. In addition, the seasonal distribution for motor vehicles used in this study reflects the regional traffic patterns as determined by the Maricopa Association of Governments. Similarly, variations in emissions from these sources during the day are estimated from typical variations in these sources' operations. For example, automobile traffic peaks during the morning and evening commuting periods, with much lower traffic volumes late at night.

4.0 IDENTIFICATION OF HAZARDOUS AIR POLLUTANTS IN ARIZONA

As was mentioned in Section 1, the research program is focusing on those hazardous substances that are likely to be present in the atmosphere in the four study regions. The development of the Research HAPs List was the first step in identifying those substances, which are referred to as chemicals of interest (COI). The Research HAPs list, which contains 676 substances or substance classes, is in Appendix D.

A screening process using the emissions estimates developed as described in Section 3 and results of the atmospheric measurements described in Section 2 is being applied to the Research HAPs List to identify the COI. This screening is similar to the concentration/toxicity screen described in the U.S. EPA's Risk Assessment Guidance for Superfund (RAGS) (U.S. EPA, 1989). This section describes both the development of the Research HAPs List and how the screening to identify the COI is being conducted.

4.1 Development of the Research HAPs List

The Research HAPs List was developed to produce a comprehensive list of substances that are not currently regulated as criteria pollutants and that may pose adverse human health or environmental effects. This list was derived from existing air toxics programs in other states and the federal government. As a starting point, the list included the 189 HAPs regulated under Section 112(b) of the 1990 Clean Air Act Amendments (CAAA). The CAAA list was expanded based on the air toxics lists of states with established hazardous air pollutant programs. The substances on this list of possible additions were then screened for human toxicity and classified as toxic, nontoxic, or unknown toxicity at concentrations likely to be present in the atmosphere, using the methodology described below. Substances classified as toxic were added to the Research HAPs List, and substances with unknown human toxicity were placed on a Potential HAPs List.

The list of candidates for addition to the 189 HAPs in the CAAA was obtained from the National Air Toxics Information Clearinghouse (NATICH) listing of state-level acceptable ambient concentration guidelines or standards and from the ADHS Arizona Ambient Air Quality Guidelines. The lists of substances from these sources were merged and sorted to yield a comprehensive list of candidate HAPs, which included more than 1,000 compounds.

The candidate HAPs were screened for the potential to cause adverse health effects with a series of sequential steps. The first step was to identify carcinogens. Substances listed as

known or probable human carcinogens (EPA weight-of-evidence categories A, B1 or B2; U.S. EPA, 1986) in either EPA's Integrated Risk Information System (IRIS) (U.S. EPA, 1993a), the March 1993 Annual Update to the Health Effects Assessment Summary Tables (HEAST) or the July 1993 Supplement No. 1 to HEAST as known or probable human carcinogens were included on the Research HAPs List.

Next, chronic noncarcinogenic air toxicants determined by U.S. EPA were identified. EPA provides a regularly updated listing of substances with verified chronic risk reference concentrations (RfCs) in IRIS. Air concentrations at or below the RfC are considered not to pose a significant noncancer risk to a person with long-term inhalation exposure. Compounds with EPA RfCs were included on the Research HAPs list.

Occupational threshold limit values (TLVs) from the American Conference of Governmental Industrial Hygienists (ACGIH) were used next as indicators of human toxicity. Substances were included on the Research HAPs List only if a time weighted average TLV had been adopted and was less than or equal to 200 parts-per-million by volume or 5 milligrams per cubic meter. These values were chosen to eliminate substances considered toxic only at concentrations that are unlikely to be encountered in the ambient atmosphere due to routine releases.

Many substances were not classified by the previous screening steps (i.e., not classified as a human carcinogen and have no quantitative exposure limits or dose-response values). In order to ensure that substances with documented adverse human health effects were included on the Research HAPs List, a substance was added to the research list if such effects are reported in the Handbook of Toxic and Hazardous Chemicals and Carcinogens (Sittig, 1991). Compounds which have no EPA or ACGIH health guidance values, or for which no adverse human health effects were reported in Sittig (1991), were retained on the Potential HAPs List.

Thus, the process actually produced two lists – a Research HAPs List, containing substances considered toxic; and the Potential HAPs List, containing substances whose toxicity might be determined in the future if more data become available.

4.2 Identification of Chemicals of Interest

The screening process described below is being conducted separately for each of the geographic regions. Therefore, the COI will likely differ from region to region because of differences in the HAPs found to be present or emitted in each region.

The first consideration in screening the Research HAPs List is whether or not a quantitative toxicity value (numerical estimates of toxicity, called "dose-response" values, that are required inputs in a quantitative risk assessment) are available for each HAP. Currently, toxicity values are not available for the majority of the members of the Research HAPs List. Because the schedule and budget constraints within which the research program must operate do not allow for development of new toxicity values, only those chemicals on the Research HAPs List with existing toxicity values are considered for inclusion as COI. Sources of dose-response values used in the screening steps and the risk assessment are discussed in Section 6.1.

Secondly, substances that have not been detected in the atmosphere during the atmospheric measurements or that have not been determined to be emitted into the air in a region are excluded from further analysis. The substances then remaining on the Research HAPs List, for which either emissions estimates or measured concentrations or both are available, are subjected to additional screening, as described below.

In order to compare the potential for adverse human health effects based on the emissions data, an estimate of the comparative toxicity of the emissions are needed. Some substances that are emitted in high amounts but that have relatively low toxicity may have the same potential for adversely affecting human health as highly toxic substances that are emitted in relatively low amounts. Therefore, emissions estimates are being weighted based on toxicity by using available carcinogenic, chronic non-cancer and acute dose-response values. The results provide semi-quantitative indicators, termed here "emission-risk indicators" (ERI), of the relative potential risks from HAPs emitted in a region.

Specifically, the weighting is being performed as follows. For potential carcinogens, higher cancer dose-response values (called "unit risk estimates") are associated with greater toxicity. Therefore, multiplying the estimated emissions of a HAP by its unit risk estimate provides its cancer ERI.

The weighting for noncarcinogens (for both chronic and acute effects) is similar. However, because the dose-response values for noncarcinogens (reference concentrations, defined above in Section 4.1) define the safe threshold concentration for exposure, lower thresholds correspond to greater toxicity. Therefore, the non-cancer ERI is calculated by dividing the estimated emissions by the non-cancer dose-response value.

Ranking the cancer ERI from highest to lowest results in a ranking of the HAPs from those for which there is a high level of concern about potential carcinogenic human health effects to those for which there may be less concern. A similar determination is made for

noncarcinogenic and acute health effects by ranking the noncancer and acute ERIs, respectively, from highest to lowest.

In addition to the emissions ranking, the atmospheric concentrations of each HAP measured in each study region are averaged over the duration of the measurement program. These average values are then multiplied by available carcinogenic dose-response values and divided by chronic and acute non-carcinogenic reference concentrations, similar to the screening applied to emission estimates. The resulting products for carcinogenic dose-response provide an estimate of the excess lifetime cancer risk (ELCR) associated with exposure, and are ranked from highest to lowest. The resulting ratios for non-carcinogenic reference concentrations, referred to as hazard quotients (HQ), provide an estimate of noncancer hazard, and are also ordered from highest to lowest. This ranking is done separately for carcinogenic and non-carcinogenic effects.

The ranking tables thus generated are being reviewed to identify the COI. Generally the emissions ranking is being used as the primary means of identifying COI, and the monitoring data are being reviewed to ensure that all major potential contributors to risks are included as COI.

5.0 ESTIMATION OF ATMOSPHERIC CONCENTRATIONS

Estimates of atmospheric HAP concentrations in each of the study regions are needed to evaluate the exposures of the population and the resulting health risks. Evaluations of chronic exposures require estimates of annual average concentrations, while estimates of acute exposures require estimates of hourly average concentrations. Additionally, estimates of sub-chronic exposures to agricultural chemicals in the Casa Grande region require monthly average concentrations. Because people do not spend all of their time at a single location, these estimates are needed throughout each region. Additionally, estimates are being made of exposures to HAPs that have settled onto the ground in Phoenix, so estimates are also needed of the concentrations of HAPs in soils.

The atmospheric measurements that are being made in a residential neighborhood in each region (see Section 2) are being analyzed to characterize concentrations of some of the HAPs. However, a full year of data is only available in the Phoenix region, so annual average concentrations in the other regions cannot be estimated by simply averaging the measured concentrations. Additionally, concentrations are not expected to be uniform within the regions, because HAP emissions and the atmospheric processes that determine how the emissions are transported and dispersed in the air vary with time and location. It is not feasible to account for this variability by measuring concentrations of all of the HAPs of concern at several locations within each region, and furthermore, currently available measurement techniques cannot quantify all of the HAPs. Therefore, the research program is also employing an atmospheric simulation model and various data analysis techniques to estimate atmospheric concentrations to supplement the results from the measurement program.

5.1 Approaches to Estimating Concentrations

The specific approach that is used to estimate concentrations depends on the geographic region and on the type of HAP:

- The atmospheric simulation model is being used to estimate annual-average concentrations of gaseous HAPs from all emission sources and of particulate HAPs from point sources in the Phoenix and Tucson regions.

- Concentrations of particulate HAPs measured at several locations as part of ADEQ's long-term visibility monitoring in Phoenix and Tucson are being analyzed to estimate

annual-average concentrations of HAPs from sources of resuspended dust, such as construction activities and vehicle-raised street dust. This approach is being used because emissions of particles from these activities are not well understood, which leads to uncertainties in the emission estimates and, in turn, in the results of the simulation modeling.

- Because the only measurements of HAP concentrations in the Casa Grande region are from the research program, the atmospheric simulation model is being used to estimate annual-average concentrations of all HAPs of interest in that region, including HAPs from sources of resuspended dust.

- The atmospheric simulation model is not expected to perform well for the Payson region because of the complex winds and mixing in the atmosphere caused by the local terrain. Therefore, concentrations in Payson are being estimated by analyzing the data from the atmospheric HAP measurements, in conjunction with data from ADEQ's State Implementation Plan (SIP) PM_{10} monitoring in Payson.

- Because all of the atmospheric HAP measurements are averages over 24-hour periods, the measured concentrations cannot be used to estimate the hourly-average concentrations needed to evaluate risks from acute exposures. Therefore, the atmospheric simulation model is being used to estimate hourly-average concentrations in Phoenix, Tucson and Casa Grande.

- Multimedia fate and transport models are being used to estimate concentrations in soils from HAPs that have settled to the ground in Phoenix.

5.2 Atmospheric Simulation Modeling

The atmospheric simulation model being used for the research program is an adaptation of a simulation model called the Acid Deposition and Oxidant Model (ADOM), that was developed previously to simulate acid deposition and ozone formation in North America (Pai, Karamchandani and Venkatram, 1995). It simulates the effects on atmospheric concentrations of dispersal of emissions in the region by winds and atmospheric turbulence and the settling of particles to the ground. Although some HAPs can be either formed or lost by chemical reactions that take place in the atmosphere, similar to the reactions that form ground-level ozone, the details of these reactions are not understood well enough, in general, to include them in the simulations. Appendix E describes the model and its application in the research program in detail.

In order to estimate both acute and chronic exposures, the simulations are being made for every hour of a year. The model requires estimates of HAP emissions throughout the region during the entire year as well as measurements of various meteorological data. The simulations are being made for 1994, because that is the most recent year for which these meteorological data are available.

The simulations are made for rectangular areas, called "modeling domains", surrounding each geographic region. Figure 5-1 shows the boundaries of these domains for the research program. The Phoenix (PH) and Tucson (TC) domains contain the urbanized portions of Maricopa and Pima counties, respectively. The Casa Grande (CG) modeling domain contains the community of Casa Grande and a substantial portion of the agricultural areas that surround it. The larger rectangle in the figure that surrounds all of the modeling domains is the overall region for which emissions have been estimated.

The model is called a "grid model", because it works by dividing the atmosphere over the modeling domain into imaginary "boxes", which are called "grid cells". The size and the number of these grid cells vary among the regions. They are 4 km (about 2-1/2 miles) on a side in the horizontal (i.e., north-south and east-west) directions for the Phoenix and Tucson regions, and 2 km (about 1-1/4 miles) on a side for the Casa Grande region. The height of each box depends on atmospheric mixing conditions. Boxes near the ground are shallower (about 40 m, or 125 feet, deep). Higher boxes are progressively thicker up to the top of the model, which is 6 km (about 19,000 feet) above the ground. Table 5-1 contains descriptions of the modeling domains, including the sizes of the grid cells and the sizes of the domains.

TABLE 5-1

Descriptions of Atmospheric Modeling Domains

Region	Grid Cell Size (km)	Number of Grid Cells (E-W x N-S)	Size of Domain (km; E-W x N-S)
Casa Grande (CG)	2 x 2	32 x 16	64 x 32
Phoenix (PH)	4 x 4	32 x 24	128 x 96
Tucson (TC)	4 x 4	10 x 10	40 x 40

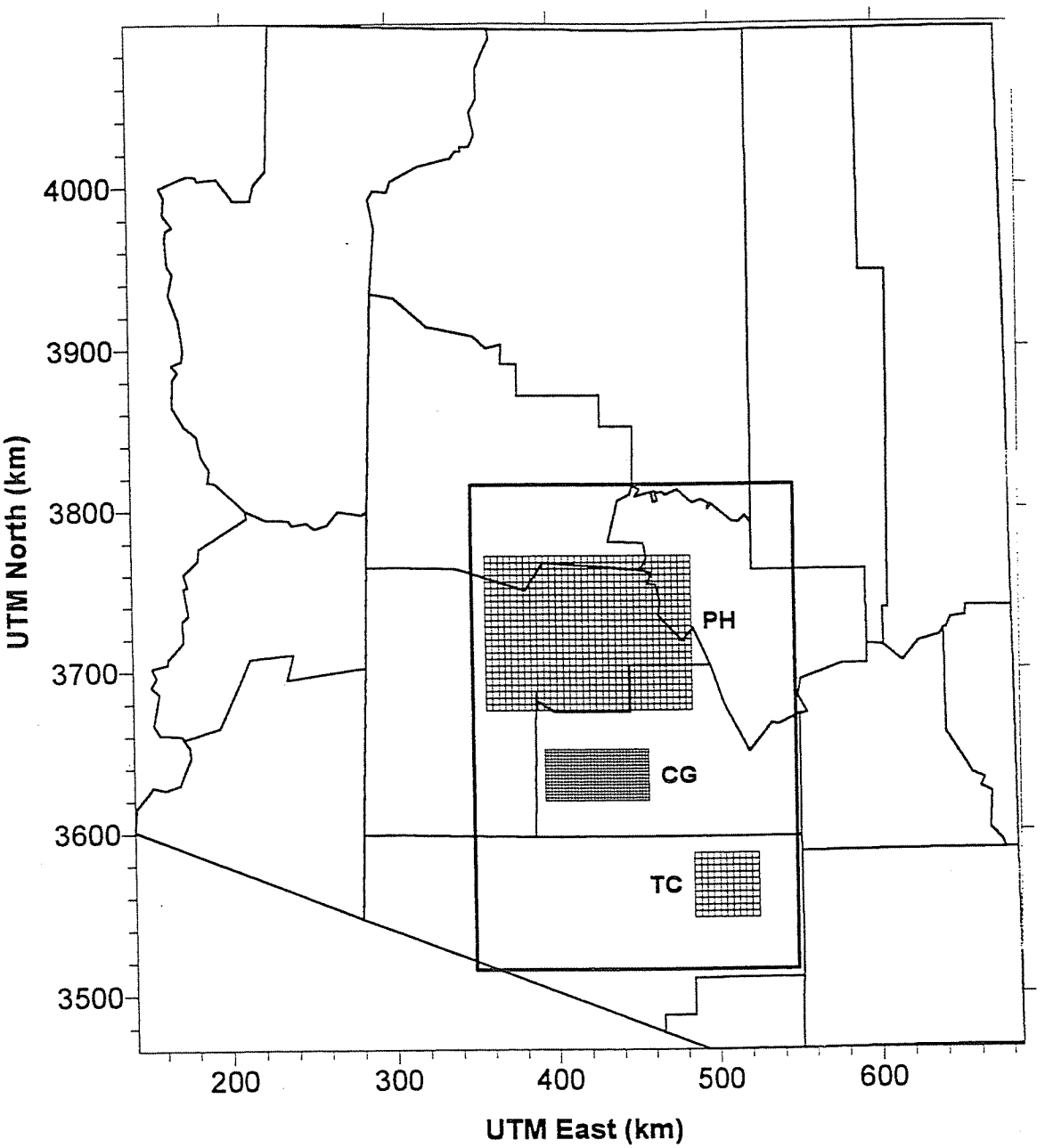


Figure 5-1 Modeling Domains and Grids

The model estimates HAP concentrations in each grid cell during each hour of a full year by calculating:

- Emissions of HAPs into the grid cell
- Movement of HAPs into and out of the grid cell by winds
- Movement of HAPs into and out of the grid cell by turbulence
- Loss of HAPs that are in particles by settling to the ground

The HAP concentrations at the outer edges of the modeling domains are set to zero, because the domains enclose the major HAP emissions in the regions. Thus, the model actually simulates HAP concentrations produced by emissions within the regions. Because there are "background" levels of HAPs in the air surrounding the regions, these background concentrations, estimated as the average concentrations measured at the Hillside regional background site (see Section 2), are added to the concentrations from the simulations.

The ability of the model to simulate 24-hour HAP concentrations accurately is being evaluated by comparing predicted concentrations with the 24-hour HAP measurements made during 1994 at the Phoenix residential neighborhood site. Because HAP measurements began in Tucson and Casa Grande during 1995, it is not possible to make similar comparisons for those regions.

The ability of the model to simulate geographic distributions of annual-average HAP concentrations is being evaluated by using carbon monoxide (CO) as a tracer for HAP emissions from motor vehicles. Motor vehicles are the dominant emitters of CO, which is measured continuously at nine locations in Phoenix by the Maricopa County Environmental Services Department. They are also the dominant emitters of several HAPs, such as benzene. Concurrent measurements of HAPs and CO were made during several days at the Indian School Road site, which is located adjacent to a heavily travelled street in Phoenix (see Section 2). The results of those measurements have been analyzed to determine the amounts of these motor-vehicle dominated HAPs that are emitted relative to CO. These relationships are then being applied to annual-average CO concentrations at the nine sites in Phoenix to estimate annual-average concentrations of the motor-vehicle HAPs at those locations. These annual-average HAP concentrations are being compared with annual-average concentrations predicted by the simulation model.

Although HAP concentrations were not measured in Tucson during 1994, estimates are being made of annual-average concentrations at the research program measurement site during 1994 for comparison with the simulation model results. The Pima County Department of Environmental Quality measures CO continuously at several locations in Tucson. Under the assumption that CO emissions are fairly constant over periods of a month or more, the differences between annual average CO concentrations during 1994 and during the period of the HAP measurements in 1995 should be indicative of differences in the dispersal of emissions in the Tucson region. Therefore, the annual average CO concentrations measured during 1994 are being divided by the average CO concentrations measured during the research program HAP measurement periods in 1995 to calculate a "scaling" factor. The average HAP concentrations measured during 1995 are being multiplied by this scaling factor to estimate 1994 annual average HAP concentrations for comparison with the simulation results.

Preliminary results from simulations in Phoenix have indicated that the simulation model predicts 24-hour average concentrations of some HAPs at the residential neighborhood site fairly well. There were systematic differences (i.e., consistent over- or under-prediction) for other species, which probably reflect uncertainties in the emission estimates. In order to compensate for these uncertainties, the simulation results for each measured HAP are being multiplied by a HAP-specific constant value, so that the predicted and measured concentrations agree on average (i.e., the average concentration measured at the Phoenix residential neighborhood site from April through December, 1994, agrees with the average concentration predicted for that location). It is assumed that these systematic differences are consistent over the entire geographic region, so the same adjustment is made for all simulation results throughout the region.

5.3 Analysis of Atmospheric Measurements in Phoenix and Tucson

As was mentioned previously, there are large uncertainties in estimates of emissions of particles from activities such as construction and paved- and unpaved-road travel that suspend dust into the atmosphere. This suspended dust usually contains HAPs that occur naturally in soil, such as cadmium and manganese. The uncertainties in the emission rates of the particles containing these HAPs could lead to large uncertainties in atmospheric concentrations from the simulation model. Therefore, the research program is analyzing measurements of HAPs in particles to estimate atmospheric concentrations for use in estimating exposures.

ADEQ is operating long-term visibility monitoring networks in Phoenix and Tucson, which include sampling and chemical analysis of PM_{10}. The chemical analyses include several of

the HAPs that are present in soils and street dust. The research program is using these measurements, along with the measurements at the residential neighborhood HAP measurement sites, to estimate atmospheric concentrations of these HAPs in these two regions.

5.4 Analysis of Atmospheric Measurements in Payson

The atmospheric simulation model would not be expected to perform well in Payson, because of the complex winds and atmospheric mixing caused by the complex terrain in the region. Therefore, the research program is analyzing the atmospheric HAP measurements that are being made there to estimate atmospheric concentrations. Because of the small size of the region, it is expected that this use of data from a single location will provide a representative estimate of concentrations for evaluating exposures and health risks.

HAP measurements began in Payson in January, 1995, (see Section 2), so a full year of concentration data are not yet available. In particular, very few measurements were made during the colder periods of the year, when HAP emissions from wood burning would be the greatest.

Although HAPs have not been measured for a full year, ADEQ operates a particulate matter sampler in Payson as part of the State Implementation Plan for the region. Samples collected with this sampler, during the second half of 1994, are being analyzed for chemical constituents that are not HAPs, but that can be used in a technique called "receptor modeling" to estimate concentrations of HAPs from wood burning.

Basically, receptor modeling uses certain chemical elements as "tracers" for emissions from specific types of emission sources. In particular, wood burning emits potassium, which is taken up by trees from soil when they grow. If potassium was emitted only by wood burning, the concentration of potassium[1] in the atmosphere could be divided by the fraction of potassium in wood burning emissions to estimate the total concentration of wood burning emissions in the air. This "total" wood burning concentration could then be multiplied by the fractions of individual HAPs in wood smoke to estimate the concentrations of the HAPs in the atmosphere.

The situation is complicated by emissions of potassium by other types sources, particularly suspended soil dust. However, there are other chemical elements, such as silicon, aluminum

[1] These analyses of the measured concentrations utilize values that are corrected for "background" levels. This correction is made by subtracting concentrations measured at the Hillside regional background site (see Section 2).

and iron, which can serve as tracers for the soil dust in the air. By knowing the fraction of these soil dust tracers in soil dust emissions, the total soil dust concentration in the air can be estimated. This total soil dust concentration can then be multiplied by the fraction of potassium in soil dust emissions to estimate the potassium in the air that is from soil dust. This soil dust potassium is then subtracted from the total amount of potassium measured in the air to estimate the amount of potassium in the air that is from wood burning. This wood burning potassium is then used to estimate HAP concentrations from wood burning as described in the previous paragraph.

Wood burning is not the only source of HAPs in Payson. Motor vehicles, commercial activities and domestic activities also emit HAPs. The atmospheric measurements during the first half of 1995 provide estimates of concentrations of HAPs from these other activities. In order to estimate average concentrations for a full year, the results from the receptor modeling for wood burning are being used with the estimates of wood burning emissions, developed as described in Appendix C, to derive a "scaling factor" that accounts for the atmospheric dispersal and mixing during the year. This scaling factor is calculated by dividing the annual-average concentrations of HAPs from wood burning by the annual HAP emissions from wood burning. Annual emissions of HAPs from other types of sources are then multiplied by this scaling factor to estimate annual-average atmospheric concentrations.

5.5 Multimedia Modeling

Modeling of the fate and transport of HAPs in the Phoenix region also includes estimation of that amounts of HAPs that deposit (i.e., settle) onto the soil. The chemicals considered for this analysis are selected based on multimedia toxicity (i.e., potential to cause health effects through pathways other than inhalation) and on deposition tendencies (e.g., chemicals in particles, such as metals and divalent gaseous mercury, $Hg^{II}(g)$). Since health effects generally result from chronic multimedia exposures, the concentrations of interest are annual averages.

Another multimedia pathway, deposition of HAPs to bodies of water that are used for recreation, fishing, or drinking water, is not being evaluated in this study. Significant water bodies are well-removed from the urban portions of the Phoenix region, where HAP are emitted, and we do not have sufficient information on airborne HAPs concentrations in those areas to perform a meaningful analysis without measurements.

In order to enter the human body through pathways other than inhalation, the chemical of interest has to be removed from the atmosphere and be deposited on soil, vegetation, or water. For deposition in the absence of rain (called "dry deposition"), this is estimated by

applying a parameter (called "deposition velocity"), that varies with the chemical species and particle size and that is obtained from the scientific literature. Deposition during rainfall (called "wet deposition") is not being considered, because rainfall occurs very infrequently. Long-term weather data indicate that precipitation occurs on average during 0.7% of the year, or only 61 hours. Therefore, relative to the dry deposition that takes place all year, wet deposition is not likely to be a major transfer mechanism for most HAPs.

These deposition rates are combined with estimates of the ability of the chemical species of interest to infiltrate the soil, which results in estimates of chemical concentrations in the soil. The concentration near the surface is used in the estimation of human exposure through skin contact with soil, and the concentration below the surface is used in the estimation of chemical uptake through the roots of vegetation.

6.0 EXPOSURE ASSESSMENT AND RISK CHARACTERIZATION

Key products of the HAPs research program will be estimates of the risks to the health of residents of Arizona because of exposure to hazardous air pollutants. These risks are being assessed in each of the four regions for both current conditions and under the conditions expected to prevail in the future.

Human health risks are being estimated by a well-established quantitative human health risk assessment approach. The National Research Council (NRC) has developed a four step paradigm for conducting human health-based risk assessments (NRC, 1983, 1994), as follows:

1. Identify the Hazard. Select chemical compounds for which a quantitative risk assessment should be performed because of their toxicity, prevalence, mobility, and/or persistence.

2. Assess Toxicity. For the selected compounds, determine the relationship between the magnitude of exposure (dose) and the occurrence of specific health effects (response).

3. Assess Exposure. Determine the magnitude and frequency of potential human exposure to the compounds of interest.

4. Characterize Risk. Estimate potential risks to human health by combining the information in the toxicity assessment and the exposure assessment.

In this process, risks are determined separately for cancer-causing substances (carcinogens) and for those that are toxic but do not cause cancer (noncarcinogens). Also, risks are determined separately for the different pathways through which the compounds of interest enter the body. The principal pathway of concern in this research program is inhalation of ambient air, that is, breathing of air with pollutant concentrations corresponding to outdoor air in areas accessible to the public. Risks due to exposure to HAPs by other pathways, such as skin contact, and eating, are expected to be much smaller than those due to inhalation, but this assumption will be tested by evaluating risks due to multimedia pathways in the Phoenix area.

Before addressing the risk assessment process in more detail, it is useful to put the information that has been presented in previous sections of this report into the four-step framework given above. The development of the Research HAPs List and the selection of compounds of interest (COI) constituted the hazard identification step and were described in Section 4. The other activities described in Sections 2, 3, and 5, namely, the selection of the study regions, the ambient air monitoring program, the emissions estimation and the estimation of atmospheric concentrations, are all aspects of the exposure assessment step.

In this section we describe the research program's techniques for performing the toxicity assessment, completing the exposure assessment, and carrying out the risk characterization. A detailed discussion of the toxicity assessment, exposure assessment, and risk assessment processes being used in the research program is contained in Appendix F.

6.1 Toxicity Assessment

The purpose of the toxicity assessment is to identify the types of adverse health effects that the COI may potentially cause, and to define the relationship between the dose of a COI and the likelihood or magnitude of an adverse effect (response). Adverse effects are characterized as carcinogenic or noncarcinogenic.

For the Arizona HAPs research program, we are using quantitative information on dose-response relationships that has been published by the U.S. EPA and the California EPA (for detailed references see Appendix F).

6.1.1 Carcinogenic Dose Response

Data on the chemical causes of cancer in humans is limited. Therefore, the potential for causing cancer in humans is usually inferred from experiments with laboratory animals. Cancer potency information is provided as a cancer slope factor (CSF) or as a unit risk estimate (URE).

The cancer slope factor (CSF) is the risk of contracting cancer, due to exposure to the chemical of interest, if the intake of the COI into the body is 1 milligram (mg) per day for each kilogram (kg) of body weight for every day of a 70-year lifetime. (A milligram is about 1/29th of an ounce and a kilogram is about 2.2 pounds.) Because a milligram is 1/1000 of a gram and a kilogram is 1000 grams, an alternative interpretation is that the CSF is the risk of contracting cancer if an amount equal to one-millionth of the body weight enters the body every day for 70 years. The actual risk is determined by multiplying the COI by the actual dosage that occurs. The result, which is usually a small number, is presented most

conveniently as a probability. For example, a risk of one in a million means that one case of cancer is expected to be caused by the COI (in excess of those cancers that would result anyway, in the absence of the COI), during the lifetimes of one million people.

Unit risk estimates (UREs) are another means of representing the dose-response relationship, particularly for inhalation exposures. The URE represents the probability of a person contracting cancer as a result of continuous exposure to the COI at an ambient concentration of 1 $\mu g/m^3$ for an entire 70 year lifetime. (Air pollutant concentrations are typically reported in $\mu g/m^3$. A microgram, abbreviated μg, is one-millionth of a gram of the HAP and a cubic meter is about 35 cubic feet of air.) Thus, multiplying the URE by the atmospheric concentration of the COI in ambient air provides an estimate of the risk of contracting cancer as a result of exposure to that concentration of the chemical over a lifetime.

Risk characterization for compounds with known or assumed potential carcinogenic effects is based on the assumption that there is no threshold dose below which there is no risk. This zero-threshold assumption therefore results in some finite level of risk associated with each dose, no matter how small. This assumption is a controversial one, but it is typically used in regulatory risk assessment because it maximizes the estimated risk from carcinogens, and thus results in pollution control strategies that maximize the protection of health. Because there is a great deal of uncertainty in cancer potency estimates, other assumptions are also made to maximize the protection of health.

6.1.2 Noncarcinogenic Dose-Response

Compounds that have effects that are not carcinogenic are assumed to have a threshold dose level below which no adverse effect occurs or, conversely, above which an adverse effect may be seen. The type of adverse effect, such as liver damage, change in kidney function, altered respiratory function, or a change in a blood parameter, with which the threshold dose is associated is termed the critical effect.

Just as with the carcinogenic potency factors, the potency of noncarcinogenic compounds can be expressed either in terms of doses or concentrations. Reference Doses (RfDs) and Reference Concentrations (RfCs) for chronic exposures to chemicals with noncarcinogenic effects have been developed by the U.S. EPA (see Appendix F for references). These values were derived from animal studies, were scaled to estimate the corresponding effect for humans undergoing long-term exposure to the compound of interest, and are then adjusted to represent effects on the most sensitive portions of the population. An RfD thus represents the smallest amount of the COI, in mg per kg of body weight per day, that could possibly cause the critical effect, even if daily exposures were to occur for a lifetime. Similarly, the RfC

represents the concentration of the COI in ambient air, in $\mu g/m^3$, that could possibly cause the critical effect if inhaled.

6.1.3 Acute Dose-Response

Acute health effects (i.e., health effects resulting from short exposures, possibly as short as a few seconds or minutes) can be important when considering inhalation exposures. Acute dose-response information is not readily available from the U.S. EPA, but the California EPA has recently developed acute dose-response values for a variety of chemicals that are being used in the risk assessment. Unfortunately the CalEPA information does not include acute dose-response values for all COI, and so dose-response effects for some compounds are being estimated from the Threshold Limit Values (TLVs) developed by the American Congress of Governmental Industrial Hygienists (ACGIH) for workplace inhalation exposures. The use of TLVs for this purpose is common, but has to be done carefully, and so it is being done in consultation with ADHS personnel.

6.2 Exposure Assessment

The exposure assessment estimates the amounts of COI to which humans are exposed over various periods of time. It consists of several components that lead to the calculation of an average daily dose (ADD) for chronic exposures, expressed as mass of substance per unit body weight per day for each COI by each pathway. The exposure assessment includes the following steps:

1. Receptor identification,
2. Identification of exposure pathways,
3. Definition of exposure calculation equations
4. Definition of receptor-specific exposure parameters, and
5. Definition of chemical-specific exposure parameters.

Each of these is discussed in turn below.

6.2.1 Receptor Identification

The term "receptor" refers to a hypothetical individual for whom risk to health is being evaluated in the risk assessment. The population of Arizona is made up of many people with many different habits and lifestyles. The purpose of the research program is to evaluate their potential exposures to COI on a regional basis and so, for this initial evaluation, all exposures

in the risk assessment are considered as averages over a region. In effect, we have assumed that residents of a region work and spend most of their time in the same region.

For the research program, two general classes of receptors were defined to be representative of the general population. A reasonable maximal exposure receptor, or RME, was designed to be representative of people who may have high exposures to HAPs. A central tendency case receptor, or CTC, was designed to be representative of people who may have what are considered to be average exposures to HAPs. Both the RME and CTC residential receptors are evaluated for exposures over a 70-year lifetime in three stages: as a young child aged 0-6 years, as an older child aged 6-18 years, and as an adult for the remaining period.

These receptors are not meant to depict actual or specific individuals in the populations of any of these regions, although care has been taken to select realistic attributes for each in order to make them representative of the general population. These high (RME) and average (CTC) exposure cases provide a realistic range of potential exposure to HAPs and consequently allow estimating the range of human health risks associated with those exposures.

6.2.2 Dose Calculation

Exposure to COI from inhalation, in terms of an average daily dose (ADD) per kilogram of body weight, depends on the following factors:

- Concentration of the HAP in air
- Inhalation rate
- Exposure time per day
- Days exposed per year
- Exposure duration (years)

These factors apply for chronic exposures; a similar approach is used for estimating acute exposure dosages.

State and federal guidance documents provide highly protective default values for these factors, but these defaults are intended for use in regulatory risk assessment. In order to

tailor the evaluation for the State of Arizona, as well as for the regions to be evaluated, region-specific data have been obtained from the scientific literature and from contact with officials from both state and local governments.

Using this information, parameters have been developed, in conjunction with ADEQ and ADHS personnel, for each receptor (RME and CTC), each age group (young child, older child, and adult), for the inhalation exposure pathway for each region, as summarized below. Corresponding parameters for the multimedia exposure assessment are still being finalized.

HAP Concentrations. Because both the RME and CTC receptors are intended to evaluate typical exposures within each region, and because it is assumed that people move around within a region, the HAP concentrations predicted by the atmospheric model are being averaged over the populated areas in each region and over the period of a year.

Exposure Time. Because exposure is being evaluated on a regional basis, we assume that all receptors are exposed to COI in ambient, outdoor, air via inhalation 24 hours per day while in the region. No distinction is made between outdoor and indoor air exposures.

Exposure Duration. An estimate of a residential occupancy period within a region (a regional occupancy period) is an appropriate estimator of exposure to HAPs. Using census data in the EPA regional occupancy period model, ROPSIM, we have determined that the average continuous duration of residence within a single county in the U.S. is 21 years, and the upper-bound (95th percentile) value is 59 years. Therefore, an exposure duration of 21 years is being used to evaluate the CTC receptor and an exposure duration of 59 years is being used to evaluate the RME receptor.

Days Exposed per Year. In order to provide an upper-bound estimate of exposure for the RME case, we have assumed that this receptor is exposed to air in the region for 365 days per year. For the CTC receptor, we have assumed that 2 weeks are spent outside of the region for vacation, etc. Therefore, the CTC receptor is assumed to be exposed to regional HAPs 350 days per year.

Averaging Period. For noncancer assessments, exposures are assumed to have a potential for eliciting adverse effects only during the period of exposure. Therefore, the averaging time for a noncancer assessment is the duration of exposure, which is 59 years for the RME receptor and 21 years for the CTC receptor.

For the evaluation of potential carcinogenic effects, the risk of contracting cancer within a person's lifetime is calculated based on the average daily dose during the lifetime of the receptor, taken to be 70 years.

Body Weight. The risk assessments for both receptors use the average body weight for each age group, as calculated from U.S. EPA (1985) data on body weights by age for U.S. residents. The average body weight for the young child aged 0-6 years is 14 kg (31 lbs), for the older child aged 6-18 years is 42 kg (92 lbs) and for the average adult is 70 kg (155 lbs).

Inhalation Rate. Because the receptors in this assessment are being evaluated for daily exposure to HAPs over a period of many years, rather than for exposures during defined periods of activity, inhalation rates based on basal metabolic rate are employed.

6.3 Risk Characterization

The risk characterization combines the results of the exposure assessment and the dose-response assessment for each compound of interest in order to estimate the potential for carcinogenic and noncarcinogenic human health risks from chronic and acute exposure to that compound.

Characterizations of the potential impacts of carcinogenic and non-carcinogenic compounds are approached in different ways. The difference arises because compounds with possible carcinogenic action are assumed to proceed by a no-threshold mechanism, whereas compounds that exhibit no carcinogenic effects may have a threshold, a dose below which few individuals would be expected to respond. Thus, under the no-threshold assumption, it is always necessary to calculate a risk for any compound that is present, but for compounds with a threshold it is possible to simply characterize an exposure as above or below a Reference Dose.

6.3.1 Carcinogenic Risk Characterization

The carcinogenic risk characterization estimates the upper bound likelihood, over and above the background cancer rate, that a receptor will develop cancer in his or her lifetime as a result of exposures to the HAPs evaluated as COI. Cancer slope factors for compounds with potential carcinogenic effects are multiplied by the estimated lifetime average daily doses (LADD) to estimate this risk. The LADD is used in the calculation of cancer risk because exposure and cancer risk are relevant to the lifetime of the individual. This risk is used to estimate the excess lifetime cancer risk (ELCR), which represents the probability of cancer

occurrence from the given level of exposure. ELCRs are being calculated for each potentially carcinogenic COI.

Carcinogenic risks are assumed to be additive. Therefore, for each receptor, the ELCRs for each pathway by which the receptor is assumed to be exposed are calculated by summing the potential risks derived for each compound. A total ELCR is then calculated by summing the pathway-specific ELCRs.

In order to indicate the implications of the ELCRs to the total population in each study region, the number of excess cases of cancer that might occur in the entire population there during a year will be estimated. This estimate is made by multiplying the ELCR by the population and dividing the result by the exposure duration in years.

6.3.2 Noncarcinogenic Risk Characterization

The potential for exposures to COI that result in adverse noncarcinogenic health effects is estimated for each receptor by comparing the average daily dose for chronic exposure to each compound with the Reference Dose for that compound (discussed in Section 6.1). The resulting ratio, known as the Hazard Quotient (HQ) for that compound, is a measure of the potential risk. An HQ well below one represents very low risk, an HQ = 1 indicates risk at the threshold level, and an HQ much larger than one indicates high likelihood of risk.

As an initial screen, the HQs for each COI to which the receptor is assumed to be exposed via a specific pathway are summed to yield a Hazard Index (HI) for that pathway, and a total HI is then calculated for each receptor by summing the pathway-specific HIs. A total HI of less than 1 for a given receptor indicates that no adverse noncarcinogenic health effects are expected to occur as a result of that receptor's potential exposure to COI.

In noncarcinogenic risk assessment, the toxic or critical effects of interest are diverse. For example, the magnitude of a toxic effect from exposure to a chemical that is a kidney toxin is not necessarily increased when exposure to a liver toxin occurs simultaneously. On the other hand, exposure to two chemicals that act on the liver may have combined effects, but not necessarily in a simply additive manner. Current knowledge does not allow for a quantitative evaluation of combined effects and so, as an interim approximation, HQs are often summed for chemicals that have similar toxic endpoints.

6.4 Uncertainty Analysis

There are many uncertainties in the risk assessment process. In order to make informed decisions based on risk assessment results, it is necessary to understand not only the magnitude of the risk, but what assumptions are likely to affect that outcome. An uncertainty analysis is being performed to evaluate each step of the risk assessment process and to estimate whether the assumptions used are likely to result in an over-estimation or an under-estimation of health risks.

7.0 SOURCE ATTRIBUTION

The development of recommendations for programs to control the release of HAPs into the ambient air requires estimates of the existing contributions of emission source categories to atmospheric concentrations in the four study regions. These estimates help focus the development of the recommendations on those types of sources that are estimated to pose the greatest health risks.

Although the atmospheric simulation model described in Section 5 estimates atmospheric concentrations resulting from HAP emissions, it is not practical to utilize it to estimate contributions from individual sources or source categories. Instead, the research program is utilizing two complementary techniques to attribute concentrations to source categories.

The first technique is called receptor modeling, because it utilizes measured atmospheric concentrations of several chemical species, including HAPs, to estimate source contributions. The relative amounts of certain key species serve as a "fingerprint" to detect and quantify the presence of the emissions from a specific source category in the atmosphere. In its simplest form, a particular chemical (not necessarily a HAP) may be emitted by only one type of source, while HAPs emitted by that type of source may also be emitted by several other sources. The chemical that is unique to the type of source serves as a tracer for the emissions. The amount of the tracer in the atmosphere is then multiplied by the quantities of HAPs emitted per unit amount of the tracer chemical to estimate how much the source type contributes to the concentrations of the HAPs in the atmosphere. For example, if source type "A" is the only type of source that emits chemical "C" in the region, and if source type "A" emits one-half pound of HAP "H" along with every pound of "C", then the contribution of source type "A" to "H" in the atmosphere is estimated by multiplying the measured concentration of "C" in the atmosphere by one-half. The situation is usually more complicated, because there are few chemicals that are emitted by only one type of source. However, various mathematical techniques are used to examine the amounts of several chemical species in the atmosphere simultaneously to address those situations.

The information needed to apply receptor modeling includes measured atmospheric concentrations of the chemical species that serve as fingerprints for the source types and information about the relative amounts of these species that are in the emissions. The research program has developed this "source composition" data for five types of sources, using data from the emissions-oriented sampling that is described in Section 2:

- Gasoline-fueled motor vehicle exhaust
- Diesel-fueled motor vehicle exhaust
- Evaporation of gasoline from motor vehicle engines and fuel systems
- Evaporation of gasoline from spills during refueling
- Wood combustion

The research program is applying receptor modeling to data from the atmospheric measurement program to estimate contributions of these five types of sources to atmospheric HAP concentrations at the measurement locations. Although it would be desirable to include additional types of sources in this receptor modeling, available data are not adequate to develop the required source compositions.

The second technique is that of apportionment of atmospheric concentrations of individual HAPs according to the fraction of region-wide emissions accounted for by each type of source. "Background" concentrations of the HAPs, estimated from the average concentrations measured at the Hillside background site (see Section 2) are first subtracted from the measured or estimated atmospheric concentrations. The remaining concentrations are then multiplied by the fraction of the total emissions of the HAP from each type of source in the region to estimate that source type's contributions. The apportionments from the receptor modeling are accounted for in this second technique by first subtracting the contributions to each HAP from the five source types addressed by receptor modeling.

As a hypothetical example, assume that motor vehicle exhaust accounts for 25 percent of the emissions of a HAP in a region, and that two other types of sources (source type 1 and source type 2) account for 45 percent and 30 percent of the emissions of the HAP. Assume further that the that HAP was not detected at the Hillside site and that receptor modeling estimated that motor vehicles account for 30 percent of the average measured concentration of the HAP in the region. It would then be estimated that source type 1 contributed 60 percent of the 70 percent not accounted for by motor vehicle exhaust (45 percent of total emissions divided by the 75 percent of emissions that is not from motor vehicles), or 42 percent of the atmospheric concentration. The estimated contribution from source type 2 would be 40 percent of the 70 percent that is not attributed to motor vehicles (30 percent of the total emissions divided by the 75 percent of emissions that is not from motor vehicles), or 28 percent of the atmospheric concentration.

Note that in this example that the receptor modeling apportioned 30 percent of the atmospheric concentration to motor vehicle exhaust, while motor vehicles accounted for 25 percent of the total emissions in the region. Differences such as this between the receptor modeling results and the apportionment according to relative emissions are expected to

occur for two main reasons. First, the atmospheric measurements are made at a specific location within a region, but the apportionment according to emission percentages utilizes total emissions within the region. If the distribution of emissions by type of source near the monitoring site is not the same as the distribution over the entire region, the relative influences of source types on the concentrations at the monitoring site will not be the same as the relative influences over the entire region. Secondly, there are uncertainties in the emission estimates, the source-composition data used in the receptor modeling, and in the ambient measurements. These uncertainties lead to uncertainties in both the receptor modeling results and in the apportionment according to relative emissions. Differences of this type are being examined in the research program to evaluate uncertainties in the source attribution results.

8.0 EFFECTS ON RISKS OF FEDERALLY MANDATED CONTROLS

The legislation enacting the HAPs research program called for an assessment of residual risk after the implementation of controls during the terms of the research program, i.e., by September, 1995. Unfortunately, owing to delays in the federal program, essentially no reductions in the emissions of hazardous air pollutants have been accomplished yet (regulations relating to dry cleaners being a very small exception). Therefore, at this time the "residual risk" is the same as the risk being estimated in Section 6.0.

However, given the charge to the research program to also provide options and recommendations for future programs, it will clearly be necessary to consider the effects of federally-mandated controls in the future. The 1990 Clean Air Act Amendments (CAAA) mandate reduction of HAP emissions from various industries over the next several years. Sources that emit over 10 tons per year of a given compound, or over 25 tons per year of all HAPs combined will be required to apply control technologies to reduce emissions by an estimated 90 to 95 percent. The U.S. EPA is establishing, and phasing in over the next seven years, these Maximum Available Control Technology (MACT) standards for over 179 classes or categories of sources. Once promulgated, affected sources will be given up to three years to install MACT.

Also mandated by the 1990 CAAA, sources that emit less than these threshold quantities may be subject to regulation under the Area Source Program, the goal of which is to reduce the incidence of cancer attributable to emissions from such sources in urban areas by at least 75 percent. EPA is required to conduct a research program to include ambient monitoring, source characterization, and research into atmospheric transformation and health effects. Using these data, EPA must develop a comprehensive area source strategy that identifies at least 30 pollutants posing the greatest threat to public health, and that identifies source categories or subcategories that account for at least 90 percent of the emissions of these pollutants.

Furthermore, it may be just as important to project reductions in HAPs emissions that might occur because of factors such as product substitution (e.g., TCE being phased out in favor of TCA in solvent usage), a new Maricopa County SIP, or vehicle fleet turnover and to project increases in emissions due to general population and VMT growth. Much of these projections will be rather speculative, but these factor should at least be recognized.

This estimating of remaining risks is being accomplished by first estimating HAP emission rates following implementation of the projected scenario. Next, the exposure from each HAP that was estimated during the evaluation of existing chronic risks will be scaled by the ratio of the projected and current estimated emissions. This approach assumes that changes in exposures depend only on emission rate of a substance within a geographic region, regardless of the locations of the sources for which emission changes occur. Although it is possible that source location could affect changes in exposure, the assessments of existing risks consider the exposure of the entire population within an airshed over several years. Because people are likely to spend time in many locations within a region, as described in Section 6.0, and risks are assumed to be proportional to an average dose over an individual's entire lifetime, neglecting the effects of source location should not have a significant effect on the validity of the conclusions.

The assessment of the cumulative effect on HAP emissions of various emission scenarios will be carried out with the following approach:

- Existing literature and prior studies are being reviewed to assemble a matrix of emission change factors for each of the source categories utilized.

- Once the matrix is complete, it will be applied to the estimates of current emissions by emission source and source category to simulate the effects of the projected changes.

The primary product of this assessment will be point and area source estimates of residual emissions, which will then be summed within each of the four geographic regions, and divided by similar sums of the current emissions. Current HAP concentrations in each region, estimated as described in Section 5.0, will be multiplied by the corresponding emission ratio to calculate projected concentrations. These projected concentrations will then be utilized in new risk evaluations, as described in Section 5.0, utilizing the dose-response and exposure parameters developed previously.

9.0 REFERENCES

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APPENDIX A

Research Program Planning Workshop Summary and Presentation Materials

AGENDA
Arizona Hazardous Air Pollution Research
Operational Program Planning Workshop
February 1 and 2, 1995
Phoenix, AZ

Workshop Objectives:

1. Establish a common understanding of the Research Program's goals, objectives, method of approach and limitations.

2. Define and select geographic regions to be evaluated during the Research Program.

3. Design HAP ambient measurement programs for the selected regions.

4. Develop a strategy for educating the general public about the Research Program.

5. Identify and address various technical issues.

February 1

9:00-9:10 **Welcome and Introductions** (F. Keene and S. Heisler)
9:10-9:25 **ADEQ Perspective on the Research Program** (G. Neuroth)
9:25-9:35 **Workshop Overview** (S. Heisler)
9:35-10:30 **Research Program Method of Approach**
(Purpose: ensure all have a common understanding of the approach by presenting it and addressing questions from ADEQ)
- 9:35-9:50 Program objectives and overview (S. Heisler)
- 9:50-10:05 Emissions Inventory (R. Dickson)
- 10:05-10:15 Ambient Measurements (F. Keene)
- 10:15-10:30 Atmospheric Modeling (P. Pai)

10:30-10:45 **Break**
10:45-11:45 **Method of Approach Continued**
- 10:45-11:00 Multimedia modeling (E. Constantinou)
- 11:00-11:20 Risk evaluation (L. Bradley)
- 11:20-11:30 Research program database (S. Heisler)
- 11:30-11:45 Public education (N. Hunter)

11:45-12:45 **Lunch**
12:45-1:30 **Method of Approach Continued**
- 12:45-1:00 Schedule (S. Heisler)
- 1:00-1:30 Limitations of approach (S. Heisler)

1:30-2:30 **Selection of Study Regions** (S. Heisler)
(Purpose: select and define four geographic regions for evaluating risks from inhalation and one region for evaluating risks from multimedia exposures)
- Philosophy and considerations
- Preliminary emission estimates
- Dose-response-weighted emissions
- Population
- Ambient data
- Initial suggestions for regions
- Discussion

2:30-2:45 **Break**

2:45-4:15 **Selection of Study Regions Continued**

4:15-5:00 **Public Education Strategy Working Group**
(Purpose: develop a strategy for educating the general public about the Research Program)
N. Hunter, F. Keene, S. Heisler

February 2

8:00-8:30 **Review of First Day's Results and Action Items** (S. Heisler)

8:30-11:30 **Monitoring Program Design Working Group**
(Purpose: design ambient monitoring programs for the four selected geographic regions, including number of sampling locations, species to be measured, and sampling schedules)
F. Keene, C. Fernandez, S. Heisler, G. Hunt, I. Tombach, L. Bradley, E. Fujita, B. Zielinska

11:30-12:30 **Lunch**

12:30-1:00 **Risk Assessment Issues Working Group**
(Purpose: identify responsibilities and procedures for determining values of receptor-specific exposure parameters and for estimating dose-response values for acute exposures)
L. Bradley, N. Petersen, S. Heisler

1:00-2:30 **Emissions Issues Working Group**
(Purposes: identify responsibilities and procedures for acquiring data needed to develop HAP emissions inventories for the four selected regions and develop approaches to coordinate and integrate work by the University of Arizona and the ENSR team to estimate HAP emissions from pesticide use)
R. Dickson, E. Fujita, S. Heisler, D. Broussard, R. Robbins, Maricopa County DEQ, J. Sagebiel, K. Stevens, W. Coats

2:30-2:45 **Break**

2:45-3:15 **Modeling Issues Working Group**
(Purpose: identify responsibilities and procedures for acquiring region-specific data needed for atmospheric and multimedia modeling)
P. Pai, E. Constantinou

3:15-3:45 **Database Issues Working Group**
(Purpose: determine how the Research Program database can be integrated with ADEQ's existing database systems)
S. Heisler, R. Dickson, J. Sagebiel, F. Keene, J. Hoyt

3:45-4:45 **Workshop Summary and Action Items** (S. Heisler)

Attendees
Arizona HAP Research Program Planning Workshop
February 1 and 2, 1995

Name	Organization	Telephone
Lee Bland	ADHS	602/542-7310
Lisa J.N. Bradley	ENSR, Acton MA	508/635-9500
Rhonda Broach	ENSR, Phoenix	602/234-2111
Doug Broussard	ADEQ	602/207-2325
John Burchard	ADEQ	602/207-2279
Wayne Coates	University of Arizona	602/741-0840
Elpida Constantinou	ENSR, Alameda CA	510/865-1888
Ron Dickson	Radian	916/362-5332
Steve Donnell	ADEQ	602/207-2319
Carmo Fernandes	ADEQ	602/207-2360
Eric Fujita	DRI	702/677-3311
Steve Heisler	ENSR, Camarillo CA	805/388-3775
Will Humble	ADHS	602/542-7312
Gary Hunt	ENSR, Acton MA	508/635-9500
Nancy Hunter	ENSR, Ft. Collins CO	303/493-8878
Frank Keene	ADEQ	602/207-2345
Dale Lemon	ADEQ	602/207-4487
Jess Lotwala	Maricopa County	602/506-6735
Mark McGarey	ADEQ	602/207-4145
Gary Neuroth	ADEQ	602/207-2349
Bill Oliver	Radian	916/362-5332
Prasad Pai	ENSR, Camarillo CA	805/388-3775
Norm Petersen	ADHS	602/230-5800
Randy Redman	ADEQ	602/207-2278
Rich Robbins	ADEQ	602/207-2351
John C. Sagebiel	DRI	702/677-3196
Kathy Stevens	ADEQ	602/207-2353
Ivar Tombach	ENSR, Camarillo CA	805/388-3775
Barbara Zielinska	DRI	702/677-3188

MEETING NOTES

Arizona Hazardous Air Pollution Reserach Operational Program
Planning Workshop

February 1 and 2, 1995
Phoenix, Arizona

Notes prepared by Bill Oliver, Radian and Steve Heisler, ENSR

FEBRUARY 1

ADEQ Perspective (Gary Neuroth, ADEQ)

The team was encouraged to be creative and bold in approaching the Research Program. Many assumptions will be needed and we will need to use our expertise in planning the complete effort. ADEQ is looking for guidance and direction from the consultant team. We need to draw conclusions from the study, with necessary disclaimers and caveats in describing the results. Let's work together throughout this effort.

Method of Approach

Overview and Objectives (Steve Heisler, ENSR)

The three objectives for the study are to: 1) estimate existing risks; 2) determine residual risks; and 3) identify options and recommendations for controlling health risks. John Burchard (ADEQ) asked if this order is the priority. Steve felt it is, but John questioned whether switching numbers 2 and 3 in priority would be better.

The major tasks are to conduct detailed planning for the study; make ambient HAP measurements; estimate HAP emissions; estimate atmospheric and multimedia HAP concentrations from data analysis and modeling; evaluate existing risks; evaluate residual risks; develop control recommendations; inform the public; develop a database; and prepare two reports. Because of time and budgetary constraints, The Research Program will focus on four geographic regions where risks are likely to be greatest or which are "characteristic" of portions of the state.

Emission Estimation (Ron Dickson, Radian)

The approach for developing the HAPs inventory involves five tasks: 1) Developing a source matrix, which is a list of source categories and associated HAPs; 2) developing the point source data; 3) developing the area source data; 4) developing the mobile source data; and 5) developing spatially and seasonally adjusted HAPs emissions estimates.

The Geocoded Emissions Modeling and Projections (GEMAP) system will be used to manage and process the HAPs emissions data.

Various issues related to emissions data will be discussed in the emissions working session later in the workshop. Some of these include pesticide emissions, special source categories of interest to the State, the acquisition of basic input data, communications with industry to request data, and ultimate use of the initial speciated HAPs emissions. Questions were asked about grid spacing, use of the California Air Resources Board (ARB) database, and HAPs emissions from reformulated gasoline use.

Ambient Measurement Program (Frank Keene, ADEQ)

Ambient sampling is performed by ADEQ staff, and laboratory analysis is performed by DRI for 27 semi-volatile organic compounds (SVOCs), 74 volatile organic compounds (VOCs), 7 carbonyls, and 29 PM_{10} compounds (using x-ray fluorescence (XRF) analysis for PM_{10}). Sampling techniques include evacuated stainless steel canisters for VOCs, DNPH-impreganted cartridges for carbonyls, polyurethane foam (PUF)/XAD-2 cartridges preceeded by filters for SVOCs species, and dichotomous samplers with Teflon membrane filters for PM_{10}. Both DEQ and DRI QA techniques are employed to ensure the integrity of the measurements.

The first measurements began in April 1994 at the Phoenix Super Site (PSS) in central Phoenix, where 24-hour samples are collected every 6 days from 10 am to 10 am. Sampling is also ongoing at a regional background site near Hillside, AZ (sampling every 12 days at this site from 10 am to 10 am). There are also sampling sites on both sides of the Mexican border at Nogales. In addition, three other sites have been used for collecting ambient sampling: the Indian School Road site in Phoenix, with 24-hour measurements on selected, high inversion days focused on motor vehicle impacts; Williams Air Force Base located in an agricultural area; and an attempt for near-field background sampling at Payson, which initially collected two samples. Meteorological data are collected at several of the sites. A mobile trailer just became serviceable this month and is currently at Payson collecting (microscale) residential wood smoke-dominated samples.

Atmospheric Modeling (Prasad Pai, ENSR)

The approach to atmospheric modeling will include three-dimensional, gridded meteorological and air quality modeling for the four geographic regions. Each modeling region will be approximately 100 kilometers (km) on each side with grid cells about 5 to 10 km on a side to estimate region-wide, annual average concentrations for evaluating chronic exposures. To evaluate acute exposures, a finer grid system (about 1 km) will be used within the coarse grid cell with the highest hourly-average concentration. Three to 4 vertical cells will be used, as well.
Data requirements for the air quality modeling are considerable for meteorology, land use, terrain, precipitation, and initial and boundary air quality concentrations.

Questions covered model validation and receptor modeling.

Multimedia Modeling (Elpida Constantinou, ENSR)

Multimedia modeling will be conducted for one of the four geographic regions. This region will be selected on the basis of the expected highest cumulative multimedia risk to the exposed population. Screening will be used to identify multipathway factors from inhalation risk estimates for use in this selection. Both dry and wet deposition modeling will be examined as part of this approach. In addition, surface water modeling will be performed for lakes and rivers. For the soil modeling, a 70 year exposure will be used.

Examples of key multimedia chemicals are mercury, PAHs, and dioxins. Mercury will be an important chemical considered in the deposition work because of mercury's high bioconcentration in bodies of water.

Risk Evaluation (Lisa Bradley, ENSR)

The risk assessment will cover four geographic regions for inhalation risk, with a multipathway risk assessment performed for one of the regions, as well. Both ambient measurements and the emissions estimates will be used for hazard identification; about 50 chemicals will be identified for detailed analysis. Toxicity values will be taken from U.S. EPA and CA ARB accepted values. Receptors will be identified in the exposure assessment step. We will focus on the reasonable maximum exposure (RME) rather than on the central tendency case (CTC) or the maximally exposed individual (MEI).

Exposure pathways will include inhalation, soil (both dermal and ingestion), surface water (both swimming and drinking water), fish ingestion, locally grown produce, local beef and dairy products, and mother's milk. Risk characterization will be performed for each receptor and for the exposed population in each region.

Furthermore, residual risks, those remaining after implementation of the 1990 Clean Air Act Amendments, will be examined by scaling the estimates of current risk. The estimates of risk will contain many uncertainties. It is expected that the difference between current and residual risk estimates will be more reliable than the absolute values of the individual risk estimates. A question was asked about estimating risks from chloroform exposure in swimming pools.

Development of Research Program Database (Steve Heisler, ENSR)

Current plans are to rely on existing hardware and software at DEQ. Options for implementing the database will initially be analyzed. After identifying the requirements for the database, a system will be selected, developed, tested, and installed. Training will be performed and the database will be populated. The database will cover both the emission estimates and the ambient measurement data. Plans also include simple query and reporting capabilities.

Public Education Program (Nancy Hunter, ENSR)

The purpose of this task is to educate and inform the public about Arizona's HAP research program. Both the Legislature and the general public will receive attention under the public education task. Strategies will be devised and informational materials, such as a fact sheet and a brochure, will be prepared. Similarly, briefing materials will be prepared for the Legislature. The final report Executive Summary also will be directed toward the Legislature. Other educational recommendations will be contained in the final report, as well.

Program Schedule (Steve Heisler, ENSR)

Dates were discussed for each of the elements of the Research Program, including emissions, concentration estimates, chronic and acute risk estimates, and multipathway risk values. For the first region, estimates of health risk are targeted for early to mid-August 1995. Risk estimates for the other regions are scheduled for mid- to late September. The two report dates are planned for September 1 and November 1. Questions were asked on the content of the September report to the Legislature. The consensus was that the first report would likely be limited to results from the initial tasks and upcoming plans for the complete effort.

Limitations of Research Program Approach (Steve Heisler, ENSR)

The major limitations in the current approach are:

- Dioxin will perhaps not be covered by this study;
- No treatment of atmospheric transformations;
- Four geographic areas, rather than the entire state, will be examined;
- Long term ambient measurements will not be fully addressed;
- Public education will be limited;
- Emissions of some compounds will not be quantified;
- Sources outside the state will not be evaluated;
- Data and methodological uncertainties will be important throughout each of the steps of the technical study.

Questions were asked about methods for determining background concentrations of selected compounds. A question also was asked about using the Nogales ambient data for analyzing wood smoke concentrations.

Selection of Study Regions (Discussion Leader: Steve Heisler, ENSR)

Initial work to aid in selecting the four study regions has centered on a screening effort for HAP emission estimates. Starting with the Grand Canyon Visibility Transport Commission (GCVTC) 1990 inventory, VOC and particulate matter emissions were speciated with U.S. EPA's library of speciation profiles. The emission estimates were weighted by available dose-response to calculate three "risk emission" indicators for each county in the state: carcinogenic, chronic non-cancer, and acute. It was emphasized that this initial work is based on many assumptions and contains important limitations. Maps and tables of the relative indicators by county, with and without weighting by county population, were presented.

On a relative basis, the counties with the two primary urban areas of the state (Maricopa and Pima Counties) present the highest risk emission indicators.

Various points were raised during the discussion of potential study regions:

- Phoenix and Tucson represent the highest countywide population-weighted risk indicators in the state and are appropriate regions of urban activity to study.
- In-depth study already is underway for the smelter region in Gila County. This region is probably of lower priority since it will be evaluated during this other study.
- It might be valuable to include a "low emissions area" for comparison (background) purposes.
- An area with wood smoke emissions might be appropriate to consider.
- Coal-fired power plant emissions do not appear to be a high priority for

evaluation in this study.

- Nogales is already under study and probably should not be evaluated under this study.
- Yuma might be an appropriate region because of its emphasis on agriculture (especially truck farming, and probably the largest area of agricultural burning in the state) and on pesticide applications (particularly for cotton crops). This might be a good rural agricultural area. PM10 SIP work has been conducted for Yuma. On the other hand, transport of emissions from California and Mexico will confound the analysis.
- Casa Grande has agricultural activity (especially cotton production) and is more convenient for access (between Phoenix and Tucson) than Yuma. Possible University of Arizona work near Casa Grande is also a benefit to selecting this area.
- Payson and Flagstaff are both candidates to represent high-altitude regions affected by wood smoke emissions during the winter. Flagstaff has a substantially larger population than Payson, so total emissions from wood burning in the area might be larger than in Payson. However, Payson is situated in a high-elevation (about 5000 ft. MSL) mountain valley, which leads to strong inversions and pollutant "trapping", causing higher PM_{10} concentrations than in Flagstaff, as verified by earlier ADEQ PM_{10} measurements. Because of these higher concentrations, substantial data related to emissions from wood burning have been developed, including wood burning surveys.

The concensus of the workshop participants was that the four geographic regions to be studied will be:

- Phoenix, to evaluate risks in the largest urban population center in the state
- Tucson, to evaluate risks in the second-largest urban population center in the state
- Payson, to characterize the highest risks that might be present in a high-elevation population center with substantial wood-burning emissions
- Casa Grande, to evaluate risks characteristic of a population center in an agricultural region

Public Education Working Session (Discussion Leader: Nancy Hunter, ENSR)

ADEQ has two offices that can assist with the public education program for this study. In addition, a broad comparative risk evaluation program (Arizona Comparitive Environmental Risk Program, ACERP), which includes public input as well as an assessment of HAPs, also

is underway.

ENSR's support of the public education component will include preparation of a fact sheet and a brochure describing the Research Program. Press releases could also be used to summarize and describe the planned study as well as the final reports to be submitted in the fall. Earth Day, in early April, might be a good time for releasing information to the press on the study. Informational tours also might be useful as a means for communications about the study. The sampling sites could be used as destinations for these tours.

It is probably important to prepare informational materials soon for the four communities selected for detailed analysis. This will be especially valuable for the non-urban regions (Payson and Casa Grande) selected for this study. To reduce the potential emotional aspects that could be attached to this study, it will be important to explain the reason this work is being conducted (Legislative mandate). Furthermore, the relationship of this study to other ongoing health studies needs to be explained.

Several other topics to be included in a near-term press release were suggested during the meeting. Draft materials should be ready in three or four weeks for internal review by DEQ.

It was suggested that work also be initiated on definitions of terms and descriptions of the technical work. Topics to cover include HAPs ("air toxics"), risk assessment, cancer risk values, exposed populations, sources of HAPs, and so forth.

FEBRUARY 2

Review of First Day's Results

The participants briefly reviewed the selection of the study regions and confirmed the selection. Additionally, it was pointed out later during the day by Wayne Coats of the University of Arizona that, although Yuma is the largest agricultural area in the state, the types of crops grown there (truck crops) are not completely characteristic of other agricultural areas. Therefore, Casa Grande may be more representative of risks in agricultural areas in Arizona.

Design of Ambient Monitoring Program (Discussion Leader: Steve Heisler, ENSR)

The purpose of this task is to design and implement ambient monitoring activities for the four selected study regions.

Barbara Zielinska of Desert Research Institute (DRI) presented measurement results for individual VOC, carbonyl, and SVOCs at the Phoenix Super Site (PSS). It was suggested that consideration be given to analyzing samples for ethylene dibromide (EDB) and ethylene dichloride (EDC), additives used in leaded gasoline. Acrolein, another compound of potential interest, also was discussed. This compound could be sampled with remote sensing techniques such as Fourier transform infrared spectroscopy (FTIR). Discussion was given to the use of species profiles to estimate acrolein emissions from motor vehicle exhaust. In addition, since this compound is quite photochemically reactive, there may be an issue over whether to include the compound in the inventory if it is not measured in ambient air. Furthermore, it was mentioned that only a few of the SVOCs have potency factor data for the risk assessment. Nevertheless, it was pointed out that we should still perform measurements for these individual compounds. Finally, it was mentioned that we will not be estimating health risks from compounds that are formed by secondary atmospheric reactions.

Eric Fujita of DRI described quality assurance activities for the ambient measurements, including an analysis of data and correlations among different measured compounds. In addition, tunnel measurements were recently made in Phoenix. Based on the availability of data from the tunnel study and the correlations that Eric presented, it may be possible to use some of these ambient measurements along with the tunnel results and diesel-vehicle oriented sampling (see below) to develop source profiles, primarily for motor vehicles.

Frank Keene of ADEQ mentioned that currently there are seven sampling events for the Hillside monitoring site; 17 samples for the Indian School Road site; and almost a year's worth of data collection (in mid-April) at the PSS.
Several alternatives were discussed for locating the available ambient monitoring equipment, which consists of four fixed sampling systems and the mobile system. The concensus of the workshop was that:

- Sampling should continue at the Phoenix Super Site until early April 1995, when one full year of sampling will be completed. The fixed sampling system used there will then be moved to a similar, residential-exposure site in Tucson to sample on an every-sixth-day schedule until the end of the program.

- Sampling should continue with the fixed syatem at Hillside on the every-twelfth-day schedule throughout the program.

- The fixed system that was used at the Indian School Road site in Phoenix should be relocated as soon as possible to a residential site near agricultural activities in Casa Grande to sample on an every-sixth-day schedule until the end of the program.

- The fixed syatem currently in Payson for near-field background sampling should be relocated to the site where the mobile system is currently located and sample on an every-sixth-day schedule until the end of the program.

- As soon as the fixed system is relocated in Payson, the mobile system should be used for source-oriented sampling. Initially, it will be located at a truck stop at Tonopah to characterize emissions from diesel vehicles.

In discussion of the sampling at the truck stop, it was noted that truck stops generally have a high degree of engine idling conditions. Therefore, it was suggested that observational notes be taken at the truck stop to record the number of trucks and their observed operating conditions (especially idling versus engine off versus moving trucks); this could include video taping at the site. Ambient sampling should not be performed in close proximity to the diesel refueling pumps.

It was also mentioned that there are no sampling plans for the two compounds now identified by the state as HAPs: ammonia and hydrogen sulfide. Additionally, for some metals, we will not have specific measurements of valence states for some metals, such as chromium.

In addition, the feasibility of measuring mercury and dioxin will be investigated. Samples appropriate for dioxin measurements might be collected, with the decision to analyze them based on observed concentrations of polycyclic aromatic hydrocarbons (PAHs).

Risk Assessment Working Session (Discussion Leader: Lisa Bradley, ENSR)

Acute dose-response values were discussed. Acute dose-response values have been developed by CAL/EPA for 32 compounds and more have been proposed. U.S. EPA has values for about 14 compounds. There are also ACGIH threshold limit values (TLVs), but these may not be appropriate to use. It will also be appropriate to consider sensitive subpopulations (e.g., older individuals), but these groups are probably already covered by the available dose-response values. For pesticides, acute effects may be important to consider, but there may not be acute or subchronic threshold values available for individual pesticides. A comment was made that we could possibly use ten times the chronic values for pesticides to estimate subchronic values, but this may not be consistent with U.S. EPA guidance. With respect to the time period for estimating emissions, it was recommended that the risk assessment group should specify the desired temporal periods for the emission estimates; the inventory and modeling groups will then determine if they can provide inputs for those temporal periods.

Cancer potency values for PAHs were mentioned as a topic for additional discussion. Lisa

will review the available values and decide which values to use in conjunction with DHS.

Exposure parameters were also discussed. Exposure durations (population migration information) will be used for calculating the central tendency case (CTC) of estimated risk. Population density information will be needed as will the types of water body exposures (e.g., recreational, drinking water, fish ingestion) in the region selected for multipathway risk assessment. Other exposure pathways that will be considered include beef and dairy ingestion and locally grown produce. Finally, it was suggested by DHS that the team should use its professional judgment rather than simply follow regulatory risk assessment guidelines.

Emission Inventory Working Session (Discussion Leader: Ron Dickson, Radian)

The year to be selected for the emission inventory was discussed first. It was agreed that we would use the most current information that we reasonably can for different types of sources. This will lead to a mix of years being used for the development of the inventory.

For pesticides, the University of Arizona (U of A) will take the lead on collecting and developing the activity data for pesticide applications. By mid-February, U of A will have initial information on pesticide applications. DRI will provide emission factors and U of A will provide final activity data for each reported pesticide application by the end of March.

Additional questions were whether there are any special source categories of interest to the team. It appears that different types of incinerators might be of interest to DEQ. For whole gasoline, changes in composition, including ethanol and MTBE amounts, have occurred and it would be useful to have detailed speciation for vehicle fuels. It was recommended that both gasoline and diesel fuels be sampled from several different retail distributors. Analysis should include VOC composition and sulfur content. DEQ will initiate collection of the gasoline samples and will consult with Radian on methodology for sampling and analysis.

An emissions working group was identified to advise the emissions work. Participants include DEQ, UofA, Maricopa, Pima, and Pinal counties, ENSR, DRI, and Radian.

Modeling Working Session (Discussion Leaders: Parsad Pai and Elpida Constantinou, ENSR)

The time periods for modeling were discussed. Annual average emissions will be provided for most source categories. Modeling runs will be conducted for 60 days for each of the four geographic regions. Data availability and definitions of the domain and grid system were also discussed.

Additional topics were examined for the multimedia modeling activities. To define the multimedia modeling region, consideration will be given to the locations of population centers, water bodies, and watershed areas. It is likely that Phoenix will be selected for multimedia modeling. A suggestion was made that the multimedia modeling region include Maricopa and Gila counties, but it was pointed out that inclusion of Gila County would add additional emissions sources, especially smelters, and would add complex terrain to the modeling requirements. It was concluded that a portion of western Gila County would be included for the multimedia modeling region, but that no emissions would be estimated for sources in Gila County.

APPENDIX B

ATMOSPHERIC HAP MEASUREMENT METHODS

B.0 ATMOSPHERIC HAP MEASUREMENT METHODS

B.1 Samplers

Separate samplers are utilized to collect volatile organic compounds (VOC), semi-volatile organic compounds (SVOC), carbonyls and particulate matter smaller than 10 μm aerodynamic diameter (PM_{10}).

B.1.1 VOC Samplers

The program uses three VOC samplers constructed and maintained by the Desert Research Institute (DRI) and three XonTech Model 910A VOC samplers. Both types of samplers are configured for sample collection in 6 liter SUMMA^{Tm} polished stainless steel canisters.

The DRI samplers utilize a metal bellows pump to draw ambient air through a 1/4 inch diameter PTFE sample line. The line is supported by a sampling cane for stability and moisture protection, and a particulate filter is located between the line and the pump. A flow controller maintains a flow rate of approximately 14 cm^3/min to fill the canister to a pressure of about 20 psi above atmospheric during the 24-hour sampling period, as described in U.S. EPA Method TO-14. A timer starts and stops the sampling pump at preset times and controls a solenoid valve that isolates the canister when the pump is not operating. An elapsed time meter records the sampling time. These samplers were cleaned and certified by DRI prior to field sampling.

The XonTech Model 910A samplers are similar to the DRI samplers. The major differences are: (1) the sample lines are constructed of either PTFE or stainless steel; and (2) the canisters are filled to about 15 psi above ambient pressure during the 24-hour sampling period. These samplers were originally cleaned and certified by XonTech prior to use in the research program.

B.1.2 SVOC Samplers

The program uses five Graseby Andersen Model PS-1 PUF high volume samplers to collect SVOC. Samples are collected on a Teflon-impregnated glass-fiber (TIGF) filter, that is supported by a stainless steel screen, followed by XAD-4 between two polyurethane foam (PUF) plugs, which are housed in a glass cartridge. A sampling pump pulls ambient air into the sampler enclosure and through the filter and PUF/XAD-4 cartridge. The flow rate is

adjustable by varying the voltage to the pump and is indicated by a magnehelic gauge. The sampler utilizes a timer for unattended sample starting and stopping and an elapsed time meter to record sample duration.

B.1.3 Carbonyl Samplers

The program uses four carbonyl samplers constructed and maintained by DRI and one sampler that was constructed by ADEQ. All of the samplers collect carbonyls on use C_{18} Sep-Pak cartridges containing dinitrophenyl hydrazine (DNPH).

In both sampler types, a pump draws ambient air through the DNPH cartridge, which is preceded by a 1/4 inch diameter PTFE sampling line, supported by a sampling cane for stability and moisture protection. Flow rate is measured with a mass flow meter and set with a needle valve to 0.450 liters/min at the start of each sampling period. A timer starts and stops the pump for unattended operation, and elapsed time meter records the sampling duration.

B.1.4 PM_{10} Samplers

The program uses five Graseby Andersen Dichotomous samplers. These samplers utilize a size-selective inlet to remove particles larger than 10 μm aerodynamic diameter from the sample flow. Coarse (aerodynamic diameter between 2.5 and 10 μm) and fine (aerodynamic diameter below 2.5 μm) particles are collected on separate 37 mm diameter Teflon membrane filters in each sampler. Flow rate is preset with the rotameter and needle valve. A timer starts and stops the sampler for unattended operation, and an elapsed time meter records sample duration.

B.2 Sampling Media Preparation

B.2.1 Stainless Steel Canisters

Stainless steel canisters for VOC samples are cleaned in the DRI laboratory by repeated evacuation and pressurization with humidified zero air at 140°C prior to sampling, and certified as described by U.S. EPA Method TO-14. All canisters are evacuated to -20 psi or lower prior to shipment to ADEQ in Phoenix. After sampling, the canisters are capped tightly and shipped by next-day air to the laboratory.

B.2.2 PUF/XAD Cartridges and Teflon Filters

XAD-4 resin is cleaned by Soxhlet extraction with methanol, followed by dichloromethane (CH_2Cl_2), for 24 hours. The cleaned resin is then dried in a vacuum oven at 40° C and stored in sealed glass containers in a clean freezer. The PUF plugs are cleaned by Soxhlet extraction with acetone followed by a second Soxhlet extraction with 10% diethyl ether in hexane, as described in U.S. EPA Method TO-13. Prior to sampling, XAD-4 resin and PUF plugs are loaded into the glass sampling cartridges.

The TIGF filters are cleaned by sonication in CH_2Cl_2 for 30 minutes, followed by 30 minute sonication in methanol. They then are dried, placed in clean aluminum foil, and labeled.

Each batch of precleaned XAD-4 resin and 10% of the precleaned PUF plugs and TIGF filters are checked for purity by solvent extraction and gas chromatography/mass spectrometry (GC/MS) analysis of the extracts.

All samples are shipped to ADEQ in Phoenix under refrigeration. After sampling, the filters and the PUF/XAD/PUF cartridges are placed in clean aluminum foil and stored under refrigeration during transport from the sampling site. They are shipped by next-day air in a refrigerated container to DRI and stored under refrigeration prior to analysis.

B.2.3 C_{18} Sep-Pak Cartridges

C_{18} Sep-Pak cartridges are first cleaned by slowly pushing 2 ml of HPLC grade water followed by 2 ml of HPLC grade acetonitrile through each cartridge. The cartridges are then impregnated with 2 ml of DNPH reagent, containing 0.14 g DNPH (previously recrystallized twice from methanol) and 1 ml of concentrated H_3PO_4 in 100 ml of acetonitrile. Each batch of 20 to 40 impregnated cartridges is dried overnight in a vacuum desiccator. Passive contamination during the drying process is minimized by placing in the desiccator a filter paper impregnated with acidic DNPH, which acts as a passive collector of airborne carbonyls. Once dried, the cartridges are plugged with Teflon plugs and stored in screw-top glass vials in a freezer. About 10% of the prepared cartridges from each batch are analyzed to verify background carbonyl concentrations.

All samples are shipped refrigerated to ADEQ in Phoenix. After sampling, the cartridges are capped tightly, placed in their glass containers, and stored under refrigeration while being transported from the sampling sites. The samples are shipped next day air to DRI in a refrigerated container, where they are stored in a refrigerator prior to analysis.

B.3 Sample Analysis

B.3.1 VOC Analysis

Samples from the stainless steel canisters are analyzed for volatile HAPs using high resolution capillary gas chromatography with flame ionization and electron capture detectors (Hewlett-Packard 5890 Series II), after cryogenic sample concentration in a freeze-out loop constructed from chromatographic-grade stainless steel tubing packed with 60/80 mesh deactivated glass beads. A sample aliquot (100-500 ml) is transferred from the canister to an evacuated vessel of a known volume through the freeze-loop immersed in liquid oxygen. The exact sample volume is determined from the pressure change of the vessel, using the Ideal Gas Law. The trap is then flash-heated with 95° C water and switched, via a rotary valve, to transfer the condensed NMHC into the gas chromatograph for analysis.

No Nafion permeable membrane or other moisture-removal device is used prior to concentration, since the use of such drying devices results in the loss of certain volatile compounds of interest. It can also introduce contaminants in the system and has been found to lower the total NMHC concentration by 10-20%.

The GC/FID response is calibrated in ppb carbon, using NIST Standard Reference Material (SRM) 1805 (254 ppb of benzene in nitrogen). The GC/ECD response is calibrated in ppbv using a mixture of authentic halogenated standard compounds (Supelco, Inc). Identification of individual species in the samples is based on the comparison of the linear retention time indices (RI), calculated from the chromatographic data as suggested by Van Den Dool and Kratz, with the RI values of authentic standards, as well as with RI data available in the literature.

B.3.2 Carbonyl Analysis

Carbonyls as the hydrazones are eluted from the sampling cartridges with 2 ml of HPLC grade acetonitrile and analyzed by high performance liquid chromatography (HPLC, Waters, Inc.) with UV detection at 360 nm. A 3.9 x 150 mm C_{18} column (Nova-Pak, Waters, Inc.) is used, and the gradient elution is as follows: 100% solvent A (water/CH_3CN/tetrahydrofuran, 60/30/10, v/v) for 2 minutes, linearly increasing to 100% B (CH_3CN/water, 60/40, v/v) over 10 minutes and holding at 100% B for 8 minutes.

Identifications are made based on matching the HPLC retention time with those of authentic standards. Authentic standards of DNPH hydrazones of formaldehyde, acetaldehyde, acetone, propionaldehyde, methyl ethyl ketone, cyclohexanone (internal standard),

benzaldehyde, and butyraldehyde are synthesized by adding an excess of the corresponding carbonyl compound to a saturated DNPH solution in 2N HCl. They are recrystallized from methanol and checked for purity by HPLC analysis.

The quantification of carbonyl compounds is accomplished by an external standard method, using precisely weighed amounts of the authentic hydrazone standards. A three-level calibration curve (plus blank) is constructed for each quantified hydrazone.

B.3.3 SVOC Analysis

Prior to extraction of the SVOC samples, the following deuterated internal standards are added to each filter-sorbent pair: naphthalene-d_8, acenaphthylene-d_8, phenanthrene-d_{10}, anthracene-d_{10}, chrysene-d_{12}, fluoranthene-d_{12}, pyrene-d_{10}, benzo[a]anthracene-d_{12}, benzo[e]pyrene-d_{12}, benzo[a]pyrene-d_{12}, benzo[k]fluoranthene-d_{12} and benzo[g,h,i]perylene-d_{12}. The PUF plugs are then Soxhlet extracted separately with 10% of diethyl ether in hexane (EPA Method TO-13) and the filter and XAD resin are Soxhlet extracted together with dichloromethane. The extracts are concentrated by rotary evaporation at 20° C under gentle vacuum to 1 ml and filtered through 0.45 m Acrodiscs (Gelman Scientific), rinsing the sample flask twice with 1 ml CH_2Cl_2 each time. Approximately 50 μl of acetonitrile is added to the sample, and CH_2Cl_2 is evaporated under a gentle stream of nitrogen. The final volume is adjusted to 1 ml with acetonitrile.

The sample is then analyzed by electron impact (EI) GC/MS, using a Hewlett-Packard 5890 GC equipped with a 7673A Automatic Sampler and interfaced to a 5970B Mass Selective Detector (MSD). Injections (1 μl) are made in the splitless mode onto a 60 m x 0.25 mm ID DB-5 fused-silica capillary column (J&W Sci).

Identification and quantification of the SVOC is made by multiple ion detection (MID), monitoring the molecular ion of each SVOC and deuterated SVOC. Calibration curves for the GC/MS/MID quantification are made for the molecular ion peaks of the SVOC using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. National Institute of Standards and Technology Standard Reference Material (SRM) 1647 (certified PAH), with the addition of deuterated internal standards and authentic standards of compounds not present in the SRM, is used to make calibration solutions.

B.4 Quality Assurance

The following quality assurance and quality control activities are implemented in the measurement program:

- Sample Handling - Sample chain-of-custody forms are checked and filled out when samples are received, loaded in the samplers and when the samples are shipped for analysis. The forms reflect both ADEQ and DRI handling of the samples.

- Sample Collection - Written standard operating procedures are followed during sample loading, collection and unloading. A sample log detailing sampling times, conditions and readings is maintained for each sample, along with the sample chain-of-custody form.

- Sampler Calibration - Written procedures define schedules for periodic calibrations and performance tests of all samplers. The flow rates of the carbonyl samplers are checked every sampling period. Semi-annual audits of the equipment are performed in addition to quarterly calibration checks. Samplers are recalibrated whenever they are moved.

- Sampler Cleaning - Samplers are cleaned every calendar quarter and whenever they are moved. Sample lines are purged with zero air or replaced, depending on visual appearance, at the same time. PM_{10} samplers are disassembled and cleaned with soap and water. The heads and parts are dried and sealed in plastic. The SVOC sampler heads are cleaned with acetone and sealed in aluminum foil. The VOC samplers are purged with zero air and the ports are sealed with aluminum foil. Only the sample lines are cleaned for the carbonyl samplers, since the collection cartridges are located immediately after the lines. Sampler maintenance and cleaning logs are maintained by ADEQ.

- Canister Certification - One canister out of each lot (six canisters) is filled with humidified air and analyzed on both ECD and GC/FID. The standard for rejection is 0.1 ppbC of any targeted hydrocarbon or 0.02 ppbv of any halocarbon.

- Replicates Analysis - A replicate analysis is performed on one sample set from each site each month.

- Field and Laboratory Blanks - Both SVOC and Carbonyl field blanks are shipped to ADEQ. The blanks are taken to the sampling sites and returned to DRI for analysis

following the normal sample handling and analysis procedures. Laboratory blanks are prepared and analyzed by DRI. Blank corrections are determined from the blank analyses.

- Audit Samples - The DRI laboratory routinely participates in external audits, including the EPA Photochemical Air Monitoring Station (PAMS) standard.

- Duplicates Samples - Random blind duplicate samples are collected quarterly by ADEQ using collocated samplers.

APPENDIX C

Development of Initial Emission Estimates

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1.0 INTRODUCTION

An emissions inventory is being developed as part of the Arizona Hazardous Air Pollution (HAP) Research Program. A draft inventory has been completed and is currently being reviewed and refined. The final inventory used for the research program will be completed in September of 1995.

This document presents the methods used to develop the draft inventory. The inventory incorporates emissions from most source types for four counties in Arizona. These counties include Gila, Maricopa, Pima, and Pinal. Data from the emissions inventory are used as input to an air quality simulation model, which estimates of atmospheric concentrations of hazardous air pollutants (HAPs). These atmospheric concentrations are then used to estimate human exposures to HAPs and the resulting health risks. The emission estimates are also used to attribute the atmospheric concentrations of the HAPs to types of emission sources. Four modeling regions were selected for evaluation of HAP health impacts.

The emission estimates were developed using currently available data with commonly accepted estimating techniques. Figure 1-1 presents steps in the inventory development. Emissions of HAPs were estimated in one of three ways:

- Data were gathered directly from county Air Pollution Control Districts (APCDs);
- Activity or throughput data were used with emission factors developed for specific source types; and
- Speciation profiles were applied to estimated emissions of particulate matter (PM) or volatile organic compounds (VOC).

As an example of the latter two estimation methods, we can consider benzene emissions from a hypothetical facility that has two processes, A and B. Process A is a diesel internal combustion engine with a source classification code (SCC) of 2-01-001-01. The reported fuel consumption rate for process A is 60,000 gallons per year. An emission factor

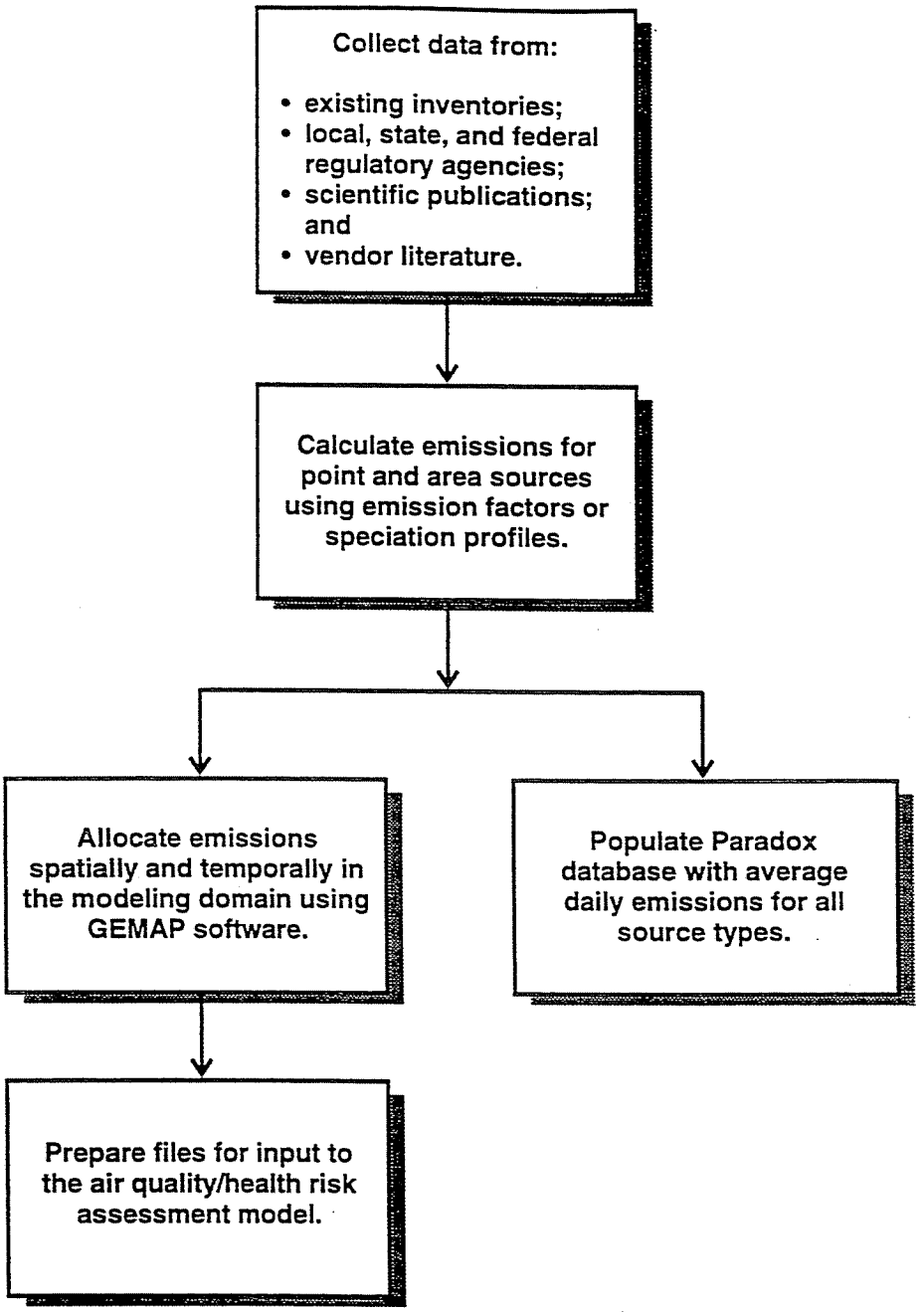

Figure 1-1. Emission Inventory Development Steps

for benzene of 0.1863 pounds per 1,000 gallons fuel is found for this particular SCC. Therefore, the benzene emissions from process A are:

$$\left(\frac{60{,}000 \text{ gals. diesel}}{\text{year}}\right)\left(\frac{0.1863 \text{ lbs. benzene}}{1{,}000 \text{ gals. diesel}}\right) = 11 \text{ lbs/yr}$$

Process B is a water-base paint application (SCC 4-02-002-10) with a reported VOC emission rate of 4 tons per year. A speciation profile for this particular SCC lists 0.36% of VOC emissions as benzene. Therefore, the benzene emissions from process B are:

$$\left(\frac{4 \text{ tons VOC}}{\text{year}}\right)\left(\frac{0.0036 \text{ tons benzene}}{\text{ton VOC}}\right)\left(\frac{2{,}000 \text{ lbs}}{\text{ton}}\right) = 29 \text{ lbs/yr}$$

Emissions estimation techniques are described in further detail in this report. The report includes the following sections:

- Section 2.0 presents the development of point source emission estimates;
- Section 3.0 presents the development of area source emission estimates;
- Section 4.0 discusses the development of on-road motor vehicle emission estimates;
- Section 5.0 describes the air quality modeling inventory development;
- Section 6.0 describes the activities that are being conducted to refine the emission estimates; and
- Section 7.0 contains references.

2.0 DEVELOPMENT OF POINT SOURCE EMISSION ESTIMATES

Point source emission estimation techniques used in developing the inventory are described below.

2.1 Point Source Identification and Emission Calculation

Point source emissions data for this inventory were obtained from three primary sources:

- Permit files maintained by local air pollution control districts (APCDs);
- The community-right-to-know reporting (i.e., EPCRA Section 313) stored in the U.S. EPA's toxic release inventory (TRI) database; and
- The Grand Canyon Visibility Transport Commission (GCVTC) inventory database, developed by Radian and containing state-derived data and 1990 U.S. EPA Interim Inventory data (Radian, 1995).

The base year for this inventory is 1993, although some of the emissions information is from other years (e.g., 1990 for GCVTC inventory data).

A decision tree used to develop emission estimates from the point source data is shown in Figure 2-1. In general, since the APCD data are the most detailed and up-to-date, they were preferentially used when emissions from a given facility appeared in more than one data source. The GCVTC point source data were used in conjunction with emission factors and speciation profiles to develop HAP emission estimates for facilities with no APCD or TRI data. Details of the data used to estimate emissions are presented in Section 2.2.

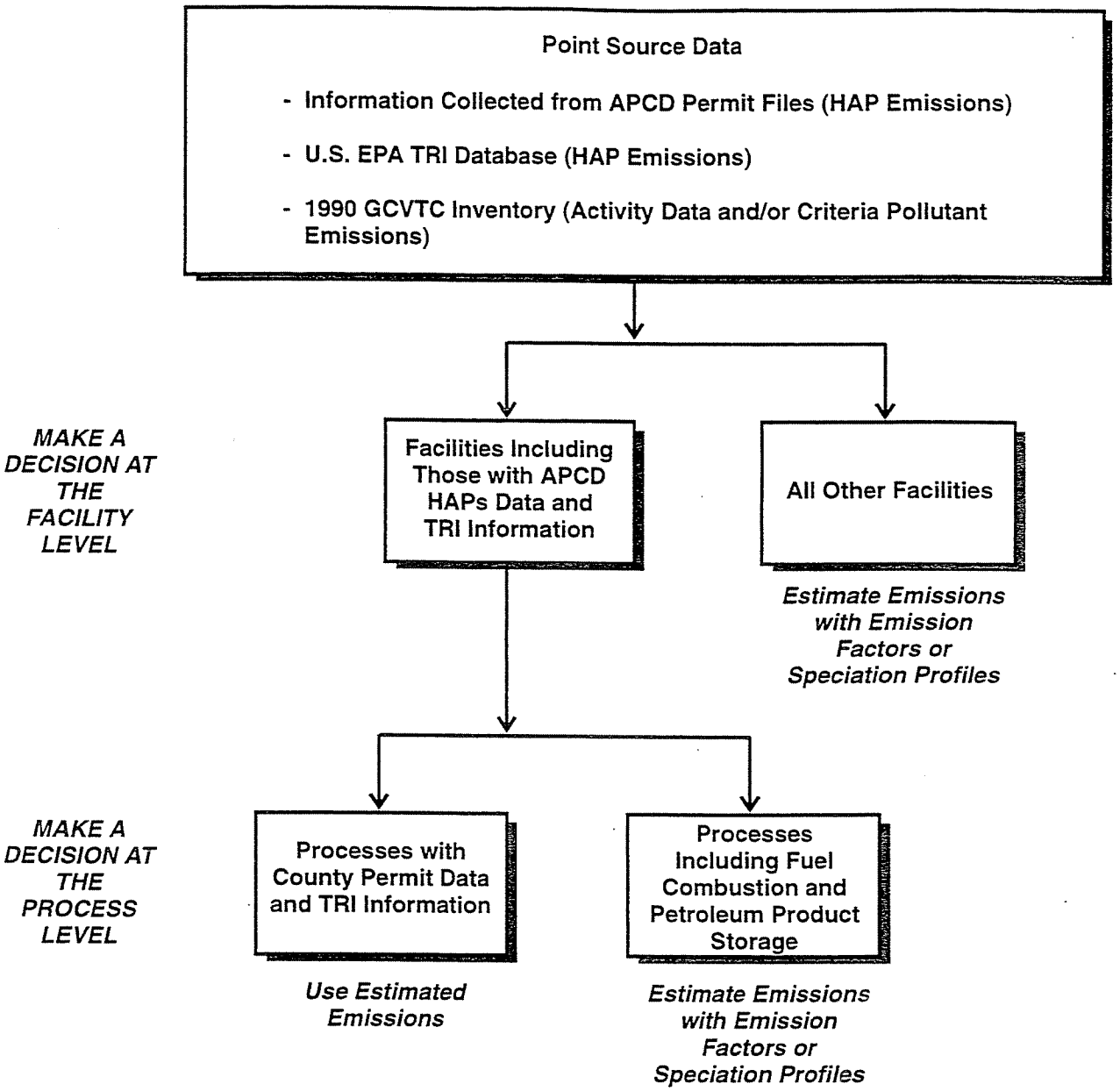

Figure 2-1. Point Source Emission Estimate Decision Tree

Table 2-1 presents an analysis of the total emissions in each county by data source (which will be completed after the emission estimates have been refined). It also lists the number of facilities for which the estimation method was used.

2.2 Point Source Data Development

Table 2-2 lists the various sources of data used to estimate emissions from point sources. The most accurate estimates of HAP emissions in the point source inventory are the estimates gathered from local APCD permit files. These data primarily represent maximum allowed solvent usage and source test results.

Maricopa County APCD supplied Radian with a list of more than two dozen facilities for which emissions of hazardous air pollutants (HAPs) could be significant. Radian staff then surveyed the permit files for these and other facilities in Maricopa County. In some cases, material safety data sheets (MSDS) were used to calculate the amount of HAPs in the solvent based on the weight fraction given in the MSDS. The emissions of HAPs were recorded and annual estimates were entered into the point source database. Pima and Pinal County APCDs also supplied Radian with emission estimates of HAPs from the significant sources in those jurisdictions. These data were likewise entered into the database.

Emissions of HAPs were also directly obtained from the U.S. EPA's TRI database. A specific list of the toxic chemicals covered under EPCRA Section 313 is contained in 40 CFR 372.65. The thresholds for reporting are based on how the toxic chemical is used at the facility. Section 313 defines the following three activities and threshold levels:

- **Manufacture** - To produce, prepare, compound, or import a toxic chemical of more than 25,000 pounds per year;
- **Process** - To prepare a toxic chemical (i.e., the incorporation of a toxic chemical into a final product) for distribution in commerce of more

Table 2-1

Distribution of HAP Emission Estimation Methods by Number of Point Sources

County	Estimation Method	Number of Facilities[a]
Gila	Generic Speciation Profile	2
Maricopa	Generic Speciation Profile	128
	APCD Permits	33
	U.S. EPA TRI Database	103
	DRI Speciation Profile	15
	Emission Factor	7
Pima	U.S. EPA TRI Database	27
	APCD Permits	1
Pinal	APCD Permits	2
	U.S. EPA TRI Database	7
	Generic Speciation Profile	10
	Emission Factor	3

[a] Some facilities may have more than one emission estimation method used, due to multiple processes with different types of data reported.

TBD = To be determined.

Table 2-2

Basis of Point Source Emission Estimates

Type of Data	Source Types	Reference
HAP emissions from permit files	Miscellaneous[a]	Maricopa County APCD
	Miscellaneous[a]	Pima County APCD
	Miscellaneous[a]	Pinal County APCD
HAP emissions from TRI database	Miscellaneous[a]	U.S. EPA TRI database
Activity data	Natural gas and diesel combustion sources	GCVTC emission inventory
Emission factors	Natural gas and diesel combustion sources	Ventura County (California) APCD
	Residual oil combustion sources	U.S. EPA FIRE database
PM and VOC emissions	All others[b]	GCVTC emission inventory
Speciation profiles	Gasoline and fuel storage	Region-specific profile developed by DRI
	All others[b]	U.S. EPA SPECIATE database

[a] Facility-wide emissions for these sources were asigned to a miscellaneous source classification code (SCC) of 99999999.

[b] Generic speciation profiles were used for any source that was not estimated by another method in this table, and had estimates of either PM or VOC in the existing GCVTC emission inventory.

than 25,000 pounds per year; and

- **Otherwise Use** - To use a toxic chemical for any activity that does not meet the definition of manufacture or process of more than 10,000 pounds per year.

If reporting is triggered, the facility must submit to the U.S. EPA a Form R (TRI Report) for each toxic chemical for which reporting is required.

The final techniques for estimating HAP emissions used both activity data (e.g., throughput, fuel consumed, etc.) and particulate matter (PM) and volatile organic compound (VOC) emission estimates from the GCVTC emission inventory. Primary copper smelters will be addressed in the risk evaluation using ambient measurements and receptor modeling. Mining activities have been included in the inventory.

Emission factors were applied only to combustion sources as shown in Table 2-2. Other source types had little or no emission factor data available. The emission factors used are shown in Table 2-3.

For all other point sources, with the exception of gasoline storage facilities, generic speciation profiles from the U.S. EPA SPECIATE database were used to estimate emissions. To develop a specific speciation profile for gasoline storage facilities, gasoline samples from three refueling stations in Phoenix were collected and analyzed. The chemical composition of the liquid gasoline was used with Raoult's law to estimate the vapor composition of gasoline. The resulting speciation profile was used for all four source regions.

Table 2-3

Emission Factors Used for Combustion Sources[a]

Pollutant	CAS Number	Source Type and Units (in parentheses)									
		Natural Gas Internal Combustion Engine <1000 hp (lb/mmcf)	Natural Gas Internal Combustion Engine >1000 hp (lb/mmcf)	Natural Gas Internal Combustion Turbine (lb/mmcf)	Natural Gas External Combustion <10 mmBTUh (lb/mmcf)	Natural Gas External Combustion 10 - 100 mmBTUh (lb/mmcf)	Natural Gas External Combustion >100 mmBTUh (lb/mmcf)	Natural Gas External Combustion Flare (lb/mmcf)	Diesel External Combustion (lb/1000 gal)	Diesel Internal Combustion (lb/1000 gal)	Residual Oil External Combustion Boiler (lb/1000 gal)
1,3-butadiene	106-99-0								0.0148	0.2174	
acrolein	107-02-8	0.3783	0.454	0.0017	0.0131	0.011	0.0022	0.0114	0.3506	0.0339	
toluene	108-88-3	1.1145	1.3374	0.1282	0.0059	0.0043	0.0013	0.0576	0.0044	0.1054	
chlorobenzene	108-90-7								0.0002	0.0002	
xylenes	1330-20-7	0.4048	0.4858	0.0298	0.0022	0.0016	0.0005	0.0576	0.0016	0.0424	
hexavalent chromium	18540-29-9								0.0002	0.0002	0.0004485
formaldehyde	50-00-0	32.4963	38.9956	0.173	0.0409	0.0296	0.0087	1.1376	0.3506	1.7261	
PAH [as B(a)P]	50-32-8	0.0179	0.0179	0.00022	0.0179	0.0179	0.0179	0.0273	0.0445	0.0362	
benzene	71-43-2	3.257	3.9084	0.01906	0.0185	0.0133	0.004	0.1152	0.0044	0.1863	
lead	7439-92-1								0.0083	0.0083	0.0003765
manganese	7439-96-5								0.0031	0.0031	0.00384
mercury	7439-97-6								0.002	0.002	
nickel	7440-02-0								0.0039	0.0039	0.051
arsenic	7440-38-2								0.0016	0.0016	0.00165
beryllium	7440-41-7								0.0016	0.0016	0.0000257
cadmium	7440-43-9								0.0015	0.0015	
chromium	7440-47-3										0.000963

Table 2-3

(Continued)

Pollutant	CAS Number	Source Type and Units (in parentheses)									
		Natural Gas Internal Combustion Engine <1000 hp (lb/mmcf)	Natural Gas Internal Combustion Engine >1000 hp (lb/mmcf)	Natural Gas Internal Combustion Turbine (lb/mmcf)	Natural Gas External Combustion <10 mmBTUh (lb/mmcf)	Natural Gas External Combustion 10 - 100 mmBTUh (lb/mmcf)	Natural Gas External Combustion >100 mmBTUh (lb/mmcf)	Natural Gas External Combustion Flare (lb/mmcf)	Diesel External Combustion (lb/1000 gal)	Diesel Internal Combustion (lb/1000 gal)	Residual Oil External Combustion Boiler (lb/1000 gal)
copper	7440-50-8								0.0041	0.0041	0.002475
zinc	7440-66-6								0.0224	0.0224	
acetaldehyde	75-07-0	0.944	1.1328	0.0173	0.0353	0.0258	0.0073	0.1138	0.3506	0.7833	
hydrogen chloride	7647-01-0								0.1863	0.1863	
selenium	7782-49-2								0.0022	0.0022	0.0006045
napthalene	91-20-3	0.1785	0.1785	0.00093	0.1785	0.1785	0.1785		0.0053	0.0197	0.001266
propylene		16.2259	19.4711	0.1824	0.2737	0.1984	0.0582	2.016	0.01	0.467	

[a] Sources of data: Ventura County APCD, 1992 and U.S. EPA FIRE database.

3.0 DEVELOPMENT OF AREA SOURCE EMISSION ESTIMATES

The development of area source emission estimates for this inventory required the performance of several steps:

- Area source categorization;
- Emission calculation method determination; and
- Area source data development.

These activities are described in detail below.

3.1 Area Source Categorization and Emission Calculation Methods

Table 3-1 lists the area source categories included in the inventory. For each area source category, an estimation method was assigned. Due to the general scarcity of HAP emission factors, the HAP emissions for most area source categories were determined by applying a speciation profile to total VOC or PM emission estimates. HAP emission factors were applied to a few area source categories, but this was usually for source categories that only had a single HAP associated with it (e.g., chloroform from swimming pools).

Table 3-1 also lists the types of data required for the estimating method, as well as a brief description of the source of these data. These data sources are described in more detail in Section 3.2, with the exception of on-road motor vehicles, which are described in Section 4.2.

Table 3-1

Arizona HAPs Inventory Area Source Matrix for Maricopa, Pima, Pinal, and Gila Counties

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Industrial Fuel Combustion (by fuel type)	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
	Emission factors (Maricopa County waste oil combustion - PM HAPs only)	Waste fuel oil usage	Maricopa County ozone SIP inventory
		HAP emission factors	AP-42
Commercial/Institutional Fuel Combustion (by fuel type)	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
Residential Fuel Combustion (excluding wood)	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Residential Fuel Combustion (excluding wood) (cont'd)	Speciation (cont'd)	PM emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
Residential Wood Combustion	Speciation	VOC emissions	Existing GCVTC emissions database/Emissions calculation based on ADEQ wood use data and AP-42 emission factors (Gila County only)
		Speciation profile	Desert Research Institute profile developed for Phoenix
		PM emissions	Existing GCVTC emissions database/Emissions calculation based on ADEQ wood use data and AP-42 emission factors (Gila County only)
		Speciation profile	U.S. EPA SPECIATE database
Highway Vehicles - Gasoline	Speciation	VOC emissions	Existing GCVTC emissions database/Emissions calculations based on ADOT VMT data and MOBILE5a emission factors (Maricopa and Pima Counties only)
		Speciation profile	Desert Research Institute profile developed for Phoenix
		PM emissions	Existing GCVTC emissions database/Emissions calculations based on ADOT VMT data and PART5 emission factors (Maricopa and Pima Counties only)
		Speciation profile	Desert Research Institute profile developed for Phoenix

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Highway Vehicles - Diesel	Speciation	VOC emissions	Existing GCVTC emissions database/Emissions calculations based on ADOT VMT data and MOBILE5a emission factors (Maricopa and Pima Counties only)
		Speciation profile	Desert Research Institute profile developed for Phoenix
		PM emissions	Existing GCVTC emissions database/Emissions calculations based on ADOT VMT data and PART5 emission factors (Maricopa and Pima Counties only)
		Speciation profile	Desert Research Institute profile developed for Phoenix
Off-Highway Vehicles/Equipment - Gasoline, 2-Stroke	Speciation	VOC emissions	Existing GCVTC emissions database/EEA Nonroad Engine Emission Inventory (Maricopa County only)
		Speciation profile	U.S. EPA SPECIATE Database
		PM emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE Database
Off-Highway Vehicles/Equipment - Gasoline, 4-Stroke	Speciation	VOC emissions	Existing GCVTC emissions database/EEA Nonroad Engine Emission Inventory (Maricopa County only)
		Speciation profile	U.S. EPA SPECIATE Database
		PM emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE Database

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Off-Highway Vehicles/Equipment - Diesel	Speciation	VOC emissions	Existing GCVTC emissions database/EEA Nonroad Engine Emission Inventory (Maricopa County only)
		Speciation profile	Desert Research Institute profile developed for Phoenix
		PM emissions	Existing GCVTC emissions database
		Speciation profile	Desert Research Institute profile developed for Phoenix
Aircraft (Military, Commercial, and Civil)	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE database
Recreational Boating (Gasoline 2-Stroke, Gasoline 4-Stroke, and Diesel)	Speciation	VOC emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE database
Railroads	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE database

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Paved Road Dust	Speciation	PM emissions Speciation profile	Pechan and Associates (Updated 1990 U.S. EPA Interim Inventory) Desert Research Institute profile developed for Phoenix
Unpaved Road Dust	Speciation	PM emissions Speciation profile	Pechan and Associates (Updated 1990 U.S. EPA Interim Inventory) Desert Research Institute profile developed for Phoenix
Chemical Manufacturing	Treat as point source	Not applicable	Not applicable
Food & Kindred Products	Treat as point source	Not applicable	Not applicable
Mineral Processes	Treat as point source	Not applicable	Not applicable
Wood Products Manufacturing	Treat as point source	Not applicable	Not applicable
Rubber/Plastics Manufacturing	Treat as point source	Not applicable	Not applicable
Oil & Gas Production	Not applicable for study regions	Not applicable	Not applicable
Windblown dust	Speciation	PM Emissions Speciation Profile	Pechan and Associates (Updated 1990 U.S. EPA Interim Inventory) Desert Research Institute profile developed for Phoenix

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Construction Processes	Speciation	PM emissions Speciation profile	Pechan and Associates (Updated 1990 U.S. EPA Interim Inventory) Desert Research Institute profile developed for Phoenix
Mining and Quarrying	Treat as point source	Not applicable	Not applicable
Miscellaneous Industrial Processes	Treat as point source	Not applicable	Not applicable
Surface Coating	Speciation	VOC emissions Speciation profile	Per capita emissions calculation using U.S. EPA Procedures Document emission factor (architectural coatings and traffic markings) Existing GCVTC emissions database/Maricopa County ozone SIP inventory/Pima County permit data (auto refinishing and other surface coating) California ARB *Speciation Manual* (architectural coatings) National Paint and Coatings Association documentation (traffic markings) U.S. EPA SPECIATE database (auto refinishing and other surface coating)
Degreasing	Speciation	VOC emissions Speciation profile	Existing GCVTC emissions database/Maricopa County ozone SIP inventory U.S. EPA SPECIATE database

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Dry Cleaning	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory/Pima County permit data
		Speciation profile (petroleum distillates and perchloroethylene)	U.S. EPA SPECIATE database
Graphic Arts	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory/Pima County permit data
		Speciation profile	U.S. EPA Procedures Document
Asphalt Application	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	California ARB *Speciation Manual*
Solvent Use - Rubber/Plastics	Emission Factors	Employment data	*County Business Patterns*
		HAP emission factor	Versar, 1989
Solvent Use - Miscellaneous Industrial	Emission Factors	Employment data	*County Business Patterns*
		HAP emission factor	Versar, 1989
Solvent Use - Miscellaneous Commercial/Consumer	Speciation	VOC emissions	Per capita emission factor calculation using U.S. EPA Procedures Document emission factor
		Speciation profile	U.S. EPA documentation for speciation of consumer/commercial solvents
Petroleum & Petroleum Product Storage	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory/Pima County permit data
		Speciation profile	Speciation profile developed by Radian and Desert Research Institute

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Petroleum & Petroleum Product Transport and Distribution	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory/Pima County permit data
		Speciation profile	Speciation profile developed by Radian and Desert Research Institute
On-Site Incineration	Speciation	VOC emissions	Existing GCTVC emissions database
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCTVC emissions database
		Speciation profile	U.S. EPA SPECIATE database
Landfills	Speciation	Methane emissions	Maricopa County ozone SIP inventory
		Speciation profile	AP-42 (volume speciation)
Wastewater Treatment	Speciation	VOC emissions	Existing GCTVC emissions database
		Speciation profile	U.S. EPA SPECIATE database
TSDFs	Speciation	VOC emissions	Existing GCTVC emissions database
		Speciation profile	U.S. EPA SPECIATE database
Pesticide Application	Emission factors	Pesticide application data	University of Arizona
		Emission factors	Pesticide-specific emission factors developed by Desert Research Institute

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Agricultural Burning	Speciation	VOC emissions	VOC emission estimates from Maricopa County ozone SIP inventory extrapolated based on total county land area and irrigated farmland area
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	PM emission estimates calculated based on information from Maricopa County ozone SIP inventory/Estimates extrapolated based on total county land area and irrigated farmland area
		Speciation profile	U.S. EPA SPECIATE database
Agricultural Tilling	Speciation	PM emissions	Pechan and Associates (Updated 1990 U.S. EPA Interim Inventory)
		Speciation profile	Desert Research Institute profile developed for Phoenix
Structural Fires	Speciation	VOC emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
		PM emissions	Existing GCVTC emissions database/Maricopa County ozone SIP inventory
		Speciation profile	U.S. EPA SPECIATE database
Wildfires and Prescribed Fires	Speciation	VOC emissions	Existing USDA Forest Service database developed for GCVTC emissions database
		Speciation profile	U.S. EPA SPECIATE database

Table 3-1

(Continued)

Area Source Category	Estimating Method	Type of Data Needed	Source of Data[a]
Wildfires and Prescribed Fires (cont'd)	Speciation (cont'd)	PM emissions Speciation profile	Existing USDA Forest Service database developed for GCVTC emissions database U.S. EPA SPECIATE database
Cooling Towers	Emission factor (hexavalent chromium)	Employee data Emission factor	*County Business Patterns* Versar, 1989
Swimming Pools	Emission factor (chloroform)	Surface area of pools Emission factor	Local pool statistics Radian study
Ethylene Oxide Sterilization	Emission factor (ethylene oxide)	Hospital bed population Emission factor	Local hospital statistics Extrapolation from HASTE
Chrome Plating	Was not estimated	Not applicable	Not applicable

[a] Existing GCVTC emissions database refers to the emissions inventory developed for the Grand Canyon Visibility Transport Commission.

ADEQ = Arizona Department of Environmental Quality
ADOT = Arizona Department of Transportation
ARB = California Air Resources Board
VOC = Volatile Organic Compounds
PM = Particulate matter
HASTE = Houston Area Source Toxic Emissions Inventory
GCVTC = Grand Canyon Visibility Transport Commission
U.S. EPA = United States Environmental Protection Agency

Versar, 1989. "Procedures for Estimating and Allocating Area Source Emissions of Air Toxics." Report prepared for the U.S. EPA OAQPS, RTP, NC.

3.2 Area Source Data Development

Table 3-2 summarizes the different sources of data required for the emission calculations and provides references for these data. As shown in Table 3-2, the most common estimation method in this inventory relies on existing total VOC and PM emission estimates in the GCVTC emissions database and then speciates these emissions using speciation profiles from the U.S. EPA SPECIATE database. This estimation method is especially common for Pinal and Gila counties. For Maricopa County, however, the GCVTC total VOC emissions were replaced by emission estimates from the 1990 Base Year Ozone Emission Inventory (or SIP inventory) that was prepared by the Maricopa County Air Pollution Control Division (APCD).

In addition to the general method described above, various other estimation methods are used for specific area source categories listed in Table 3-2. These other estimation methods and the special types of data required are explained in greater detail below.

3.2.1 Estimation of PM HAP Emissions from Fugitive Dust Sources

Updated PM emission estimates were obtained and used to replace existing GCVTC PM emission estimates for paved road dust, unpaved road dust, windblown dust, construction processes, and agricultural tilling. These PM emissions were then speciated using source-specific speciation profiles. The updated PM estimates were obtained from the recently updated 1990 U.S. EPA Interim Inventory which was provided by Pechan and Associates. Speciation profiles for these sources were obtained from the Desert Research Institute, who developed Phoenix-specific profiles from ambient data in an earlier study.

Table 3-2

Arizona HAPs Area Source Data Sources

Type of Data Needed		Reference
Existing VOC/PM Emissions	Existing emissions database	GCVTC emissions inventory
	Updated emissions estimates for Maricopa County	Maricopa County APCD. *1990 Base Year Ozone Emission Inventory for Maricopa County, Arizona, Nonattainment Area.* Phoenix, Arizona, 1993
	Updated emissions estimates for Maricopa County off-highway vehicles/equipment	Energy and Environmental Analysis, Inc. *Nonroad Engine Emission Inventories for CO and Ozone Nonattainment Boundaries Phoenix Area.* Prepared for U.S. EPA, Ann Arbor, Michigan, 1991
	Updated particulate emissions estimates	Updated 1990 U.S. EPA Interim Inventory developed by Pechan and Associates
	Pima County solvent usage data (surface coating, dry cleaning, graphic arts, and petroleum & petroleum product storage/ transport/distribution)	Pima County permit data from Mr. Doug LaGrange of the Pima County APCD, 14 April 1995
	Wildfire and prescribed fire emissions estimates	USDA Forest Service database
Activity Data	Natural gas/waste fuel oil usage and methane emissions for Maricopa County	Maricopa County APCD. *1990 Base Year Ozone Emission Inventory for Maricopa County, Arizona, Nonattainment Area.* Phoenix, Arizona, 1993
	Wood usage for Gila County	Personal communication with Mr. Phil Denee of the ADEQ, 30 March 1995

Table 3-2

(Continued)

Type of Data Needed		Reference
Activity Data (cont'd)	Population data: Maricopa (July 1994 estimate) Pima (July 1994 estimate) Pinal (1994 projection) Gila (1993 projection)	Personal communication with all four county governments, 29 March 1995
	Employment statistics	*County Business Patterns*, 1992
	Pesticide application data	University of Arizona database
	County land area and irrigated farm land area	U.S. Bureau of the Census. *County and City Data Book, 1983.* Washington, D.C., 1983
	Pool statistics for Maricopa and Pima Counties	Personal communication with Mr. Bob Van Voorhis of the Blue Energy Institute (602-274-9200) and Mr. Mark Ragel of Patio Pools (602-886-1211), 12 April 1995
	Hospital statistics	Arizona Department of Health Services listing of Arizona Medicare certified/state licensed hospitals, 1 February 1995
Emission Factors	Emission factors for waste oil combustion and residential wood combustion	U.S. EPA. *Compilation of Air Pollution Emission Factors*, AP-42, OAQPS, Research Triangle Park, North Carolina, 1993
	Emission factors for rubber/plastic solvent use, miscellaneous industrial solvent use, and cooling towers	Versar, Inc. *Procedures for Estimating and Allocating Area Source Emissions of Air Toxics*. Prepared for U.S. EPA, OAQPS, Research Triangle Park, North Carolina, 1989
	Emission factors for architectural coatings, traffic markings, and miscellaneous commercial/consumer solvent use	U.S. EPA. *Procedures for the Preparation of Emissions Inventories for Carbon Monoxide and Precursors of Ozone, Volume I: General Guidance for Stationary Sources*, EPA-450/4-91-016, OAQPS, Research Triangle Park, North Carolina, 1991

Table 3-2

(Continued)

Type of Data Needed		Reference
Emission Factors (cont'd)	Pesticide emission factors	Developed for the Arizona HAPs Inventory by Desert Research Institute using pesticide application data from the University of Arizona
	Chloroform emission factors for swimming pools	Radian Corporation.
	Ethylene oxide emission factors for ethylene oxide sterilizers	Radian Corporation. *Development of the Houston Area Source Toxic Emissions (HASTE) Inventory*. Austin, Texas, 1995.
Speciation Profiles	Generic speciation profiles	U.S. EPA SPECIATE database
	Arizona specific speciation profiles for: Residential Wood Combustion (VOC) Off-Highway Vehicles/Equipment (VOC/PM) Paved Road Dust (PM) Unpaved Road Dust (PM) Windblown Dust (PM) Construction Processes (PM) Agricultural Tilling (PM)	Developed for the Arizona HAPs inventory from ambient measurements by Desert Research Institute
	Architectural coatings speciation profile	California ARB. *Air Resources Board SPECIATION MANUAL: Identification of Volatile Organic Compound Species Profiles*, Emission Inventory Branch, 1991.
	Traffic markings speciation profile	National Paint and Coatings Association (NPCA). *Architectural and Industrial Maintenance Surface Coatings VOC Emissions Inventory Summary*. Submitted to the U.S. EPA, OAQPS, Research Triangle Park, North Carolina, 1993.

Table 3-2

(Continued)

Type of Data Needed		Reference
Speciation Profiles (cont'd)	Graphic arts speciation profile	U.S. EPA. *Procedures for the Preparation of Emissions Inventories for Carbon Monoxide and Precursors of Ozone, Volume I: General Guidance for Stationary Sources*, EPA-450/4-91-016, OAQPS, Research Triangle Park, North Carolina, 1991
	Miscellaneous commercial/consumer solvent use speciation profile	U.S. EPA. *Compilation and Speciation of National Emissions Factors for Consumer/Commercial Solvent Use*, EPA-450/2-89-008, OAQPS, Research Triangle Park, North Carolina, 1989.
	Landfill emissions speciation profile	U.S. EPA. *Compilation of Air Pollution Emission Factors*, AP-42, OAQPS, Research Triangle Park, North Carolina, 1993
	Gasoline storage/transport/distribution speciation profile	Developed for the Arizona HAPs Inventory by Radian Corporation using Desert Research Institute sampling data

3.2.2 Estimation of HAP Emissions from Off-Highway Vehicles and Equipment

Updated total VOC emissions from the Nonroad Engine Emission Inventory developed by Energy and Environmental Analysis replaced GCVTC emission estimates for gasoline (2- and 4-stroke) and diesel off-highway vehicles and equipment. These total VOC emissions were then speciated using SPECIATE profiles (non-catalyst gasoline-powered vehicles and equipment) and source-specific speciation profiles (diesel-powered vehicles and equipment). These updated emissions data were only available for Maricopa County, but the availability of additional data for Pima County is being investigated for use developing the refined emission estimates.

3.2.3 Estimation of HAP Emissions for Pima County Solvent Sources

The Pima County total VOC estimates for a number of solvent use categories in the existing GCVTC inventory were updated using permit data provided by Pima County personnel. These updated estimates included certain types of surface coating, degreasing, dry cleaning, graphic arts, and petroleum and petroleum product storage/transport/ distribution categories. These emission estimates were then speciated according to the various profiles listed in Table 3-1. For a few categories, permitted usage amounts for individual HAPs (e.g., acetone and methyl ethyl ketone) were also included in the data received from Pima County. These individual HAP amounts were added to the HAP amounts resulting from the speciation of total VOC emissions.

3.2.4 Estimation of HAP Emissions for Residential Wood Combustion

For Maricopa, Pima, and Pinal Counties, the total VOC and PM emission estimates in the GCVTC inventory provided the basis for estimation of HAPs for residential wood combustion. The emission estimates for Gila County were updated based on recent information available from ADEQ. As part of the recent PM_{10} State Implementation Plan (SIP), ADEQ personnel determined there are approximately 1,500 residences in the town of

Payson that were each burning 5 cords of wood per year. The composition of the consumed wood is estimated to be 69% juniper and 24% oak with the remainder being pine, mesquite, cedar, and mill scraps. This composition along with wood density data was used to estimate the weight of wood that was burned. Appropriate AP-42 emission factors were then applied to this wood usage data to arrive at total VOC and PM emission estimates for Payson.

The total VOC emission estimates for all four counties were then speciated using a source-specific speciation profile developed for this study by Desert Research Institute, while the PM emission estimates were speciated using a generic SPECIATE profile.

3.2.5 Estimation of HAP Emissions for Surface Coating

In general, HAP emissions for surface coating were calculated by speciating total VOC emissions using a SPECIATE speciation profile. The total VOC emissions were based upon the Maricopa County ozone SIP inventory, Pima County permit data, or the GCVTC inventory. Two exceptions to this were for architectural coatings and traffic markings. Total VOC emissions for both of these categories were calculated using a per capita emissions factor found in the U.S. EPA Procedures Document.

Information submitted by the National Paint and Coatings Association (NPCA) to the U.S. EPA indicates that 89.5% of the architectural coatings used in the U.S. were waterborne, while the remaining 10.5% are solvent-borne. This apportionment was used in the Houston Area Source Toxic Emissions (HASTE) inventory and is based on survey information collected by the NPCA. Two separate speciation profiles from CARB's *Speciation Manual* were then applied to the total VOC emissions from waterborne and solventborne coatings. The HAPs speciation for the traffic markings area source category was also derived from total VOC emissions data submitted by the NPCA.

3.2.6 Estimation of HAP Emissions for Graphic Arts

The total VOC emissions for the graphic arts area source category are based on the Maricopa County ozone SIP inventory, Pima County permit data, and the GCVTC inventory. The HAPs speciation profile is based the national average composition of printing inks that is included in the U.S. EPA Procedures Document.

3.2.7 Estimation of HAP Emissions for Asphalt Application

The total VOC emissions for the asphalt application area source category are based upon the Maricopa County ozone SIP inventory and the GCVTC inventory. The HAPs speciation profile is taken from CARB's *Speciation Manual.*

3.2.8 Estimation of HAP Emissions for Rubber/Plastic Industry and Miscellaneous Industrial Solvent Use

The estimation of HAP emissions for the rubber and plastic industry, as well as for miscellaneous industrial solvent use, involves the use of per employee HAP emission factors provided in *Procedures for Estimating and Allocating Area Source Emissions of Air Toxics*. Employment data for each county were obtained from *County Business Patterns*. The procedures document indicated the appropriate SIC codes that should be examined to derive county employment data. For the rubber and plastic industry, only those employees that were employed in SIC codes beginning with 30xx were to be counted. For the broader miscellaneous industrial solvent use category, the emission factors are based on half of the number of employees in SIC codes beginning with 19xx through 39xx plus half of the overall county employment. Individual HAP emission factors were then applied to these resultant employment numbers.

3.2.9 Estimation of HAP Emissions for Miscellaneous Commercial and Consumer Solvent Use

Per capita emission factors for room deodorants and disinfectants, glass cleaners, moth control products, personal care products, consumer adhesives, and windshield washing fluids were used to estimate total VOC emissions. These per capita emission factors were found in the U.S. EPA Procedures Document. The U.S. EPA has determined appropriate speciation profiles for each of these groups of products which are listed in *Compilation and Speciation of National Emissions Factors for Consumer/Commercial Solvent Use*. These profiles were then applied to the estimated total VOC emissions. Existing total VOC estimates in the Maricopa ozone SIP inventory were removed to prevent double counting.

3.2.10 Estimation of HAP Emissions for Landfills

The HAP emissions from landfills were calculated using methane emission estimates as the basis. Methane emission estimates were available only for Maricopa County. Methane emissions were converted from mass into a volume and then speciated according to the volume speciation presented in AP-42. Finally, these volume estimates of HAPs were then converted back to mass estimates. A lack of readily available data prevented similar calculations for the other source regions.

3.2.11 Estimation of HAP Emissions for Agricultural Pesticide Application

The HAP emissions from pesticide application were calculated through the use of pesticide-specific emission factors and applicable data. The emission factors (mass of active ingredient emitted per mass of active ingredient applied) were obtained from the Desert Research Institute. Application data were compiled by University of Arizona researchers. This database contains each individual application of pesticide reported in the four study regions.

3.2.12 Estimation of HAP Emissions for Agricultural Burning

Criteria pollutant emission estimates for agricultural burning are included as part of the Maricopa County SIP. To estimate agricultural burning emissions in the other regions, total VOC emissions were extrapolated based on the emission estimates for the Maricopa County nonattainment area and reported land use. The Maricopa emissions represent the burning of citrus trees, ditchbanks and fence rows, tumbleweeds, and general land clearance. The emissions resulting from the burning of tumbleweeds and general land clearance were extrapolated based on total county land area. The emissions from the burning of ditchbanks and fence rows were extrapolated based irrigated land area within the county. The emissions from the burning of citrus trees were neither extrapolated nor included in the non-Phoenix source regions.

The PM emissions for the Maricopa County nonattainment area are based on activity data in the ozone SIP and AP-42 emission factors. These PM emissions were then extrapolated in the same manner used for total VOC. Following estimation of total VOC and PM emissions, generic SPECIATE speciation profiles were applied to estimate HAPs.

3.2.13 Estimation of HAP Emissions for Wildfires and Prescribed Burns

The USDA Forest Service database that was developed for the GCVTC emissions data provided the initial total VOC and PM data needed to calculate HAP emissions from wildfires and prescribed burns. This database provided total VOC and PM emissions, as well as the location, for each distinct fire event from 1986 through 1992. The emissions for each fire event were summed and the totals divided by seven to obtain county-wide annual average emissions. Only one year of data for prescribed burns was available (1989), so this was taken to represent annual average emissions. These emission estimates were then also summed by county. Speciation profiles from the SPECIATE database were used to calculate HAP emissions for both wildfires and prescribed burns.

3.2.14 Estimation of Hexavalent Chromium Emissions from Industrial Cooling Towers

The estimation of hexavalent chromium emissions from industrial cooling towers involves the use of per employee HAP emission factors (Versar, 1989). These emission factors were applied to the number of employees in a county that were employed by the following industrial sectors: petroleum refining, chemical manufacturing, primary metals, textile finishing, tobacco, tire and rubber, glass manufacturing, and utilities. The employment data for each county was obtained from *County Business Patterns*.

3.2.15 Estimation of Chloroform Emissions from Swimming Pools

At ADEQ's request, swimming pools were included as an area source category. The number of pools was obtained by contacting a pool manufacturers association and a pool dealership (refer to Table 3-2). There are approximately 197,500 pools in Maricopa County, 32,000 pools in Pima County, and a minimal number of pools in Pinal and Gila Counties. The pool manufacturers' association estimated that, on average, each pool has approximately 600 square feet of surface area. Using this information, the total pool surface area was calculated. A chloroform flux measured by Radian for a study at the University of California-Davis pool was then applied to the pool surface area. It was assumed that the percentage of time that a residential pool is actually used is relatively small. As a result, it was decided that a quiescent surface flux was more appropriate than an active surface flux.

3.2.16 Estimation of Ethylene Oxide Emissions from Ethylene Oxide Sterilizers

To determine ethylene oxide emissions from hospital ethylene oxide sterilizers, the number of hospital beds at each facility was obtained and combined with an emission factor derived for the HASTE Inventory. These usage rates were derived from survey data for Houston area hospitals and then normalized by the number of beds.

4.0 DEVELOPMENT OF MOTOR VEHICLE EMISSION ESTIMATES

This section describes the source categorization, emission calculation methods, and data development used in the development of on-road motor vehicle emission estimates. Differences in calculation methods for different counties are also identified. Nonroad motor vehicles are included with the area sources discussed in Section 3.0.

4.1 Motor Vehicle Categorization and Emission Calculation Method

In general, motor vehicles in this emissions inventory consist of the following categories:

- Light-duty gasoline vehicles;
- Light-duty gasoline trucks;
- Heavy-duty gasoline vehicles;
- Light-duty diesel vehicles;
- Light-duty diesel trucks;
- Heavy-duty diesel vehicles; and
- Motorcycles (Maricopa and Pima counties only).

The motor vehicle emission calculation method differs between the more populous counties (Maricopa and Pima) and the less populous counties (Pinal and Gila). We calculated total VOC and PM emission estimates for Maricopa and Pima Counties using the U.S. EPA MOBILE5a and PART5 emission factor models. Due to different data sources, input parameters, and assumptions, there are some differences in emission calculation method between these two counties.

The total VOC and PM emission estimates for Pinal and Gila Counties were obtained from the GCVTC inventory and were not recalculated. Details of these three emission calculation methods (Maricopa, Pima and Pinal/Gila) are presented in subsections 4.1.1 through 4.1.3.

Regardless of the total VOC and PM emission estimation methods, the final step of the emission calculation method was identical for all four counties. In this step, speciation profiles developed especially for this inventory by Desert Research Institute were applied to seasonal total VOC and PM emission estimates. These speciation profiles include total VOC and PM profiles derived from ambient measurements for both gasoline- and diesel-powered motor vehicles. With the exception of total VOC speciation for gasoline-powered vehicles, speciation profiles were applied to all four seasons. For speciation of total VOC emissions from gasoline-powered vehicles, Desert Research Institute supplied both a summer profile and a winter profile. The summer profile was applied to spring, summer, and autumn emission estimates, whereas the winter profile was applied exclusively to winter emission estimates.

4.1.1 Emission Calculation Method for Maricopa County

For Maricopa County, U.S. EPA's MOBILE5a and PART5 models were used. MOBILE5a was run once for each season, whereas PART5 was run once for the entire year. The Maricopa Association of Governments Transportation and Planning Office (MAGTPO) provided input parameters and other data necessary to accurately represent the motor vehicle categories (see Table 4-1). The MAGTPO indicated that 88% of the vehicles were affected by the I/M programs. Two runs were therefore conducted for each season - one with an I/M program in place, and the other without. An overall emission factor was determined by calculating the weighted average based on this 88%/12% split. MOBILE5a was not used to calculate emissions from vehicle refueling; refueling emissions were included in the area source emission calculations.

Table 4-1

Maricopa County MOBILE5a Input Parameters

Input Parameter	Maricopa County Input Parameter
Year	1993
Tampering rates	National default rates
Vehicle miles traveled (VMT) mix	National default VMT mix
Registration distributions by age	Local registration distributions
Annual mileage accumulation rates	National default accumulation rates
Basic exhaust emission rates	National default basic emission rates
Inspection and maintenance (I/M) program	Annual, Test only, 2500/Idle test
Anti-tampering program	Annual, Inspection only
Percentage of vehicles subject to I/M program	88%
Summer RVP	7.5
Winter RVP	9.1 (MTBE oxygenated fuel); 10.1 (ethanol oxygenated fuel)
Percentage of oxygenate in oxygenated fuels	2.7% (MTBE oxygenated fuel); 3.5% (ethanol oxygenated fuel)
Percentage of winter oxygenated fuel sales	12% (MTBE oxygenated fuel); 88% (ethanol oxygenated fuel)
Sales period of oxygenated fuels	October 1 - March 31

Many of the MOBILE5a input parameters and other data were used in the PART5 calculations. The PART5 emission factors for this inventory consist of PM_{10} from exhaust, tire wear, and brake wear.

The MAGTPO also supplied VMT and other necessary activity data needed for the emission estimation process. The average daily VMT was given as 48.533 million miles per day. This value was adjusted using seasonal factors of 0.993 for winter (November through January), 1.034 for spring (February through April), 0.984 for summer (May through July), and 0.989 for autumn (August through October). The actual adjustment occurred in the temporal profiles for motor vehicles. Average daily VMT was distributed among 10 separate road classifications (urban and rural freeways, principal arterials, minor arterials, collectors, and local roads). Average vehicle speeds for each of these road types were also supplied by MAGTPO.

4.1.2 Emission Calculation Method for Pima County

MOBILE5a and PART5 were also used to estimate total VOC and PM emissions in Pima County. Like Maricopa County, MOBILE5a was run once for each season, while PART5 was run once for the entire year. The Pima Association of Governments (PAG) provided input parameters and other data necessary to accurately represent the motor vehicle categories. This information for MOBILE5a is summarized in Table 4-2.

Several input parameters differ significantly from those for Maricopa County, particularly those related to oxygenated fuels and RVP. Also, PAG indicated that I/M applied to all vehicles. Therefore, only one model run was necessary for each season. MOBILE5a did not calculate emissions from vehicle refueling, because refueling emissions were calculated as an area source.

Table 4-2

Pima County MOBILE5a Input Parameters

Input Parameter	Pima County Input Parameter
Year	1993
Tampering rates	National default rates
Vehicle miles traveled (VMT) mix	National default VMT mix
Registration distributions by age	Local registration distributions
Annual mileage accumulation rates	National default accumulation rates
Basic exhaust emission rates	National default basic emission rates
Inspection and maintenance (I/M) program	Annual, Test only, Idle test
Anti-tampering program	Annual, Inspection only
Percentage of vehicles subject to I/M program	100%
Summer RVP	9.0
Winter RVP	10.0 (MTBE oxygenated fuel); 10.0 (ethanol oxygenated fuel)
Percentage of oxygenate in oxygenated fuels	1.8% (MTBE oxygenated fuel); 1.8% (ethanol oxygenated fuel)
Percentage of winter oxygenated fuel sales	25.7% (MTBE oxygenated fuel); 74.3% (ethanol oxygenated fuel)
Sales period of oxygenated fuels	October 1 - March 31

Many of the MOBILE5a input parameters and other data were used in the PART5 calculations. Calculated PART5 emission factors for this inventory consisted of PM_{10} from exhaust, tire wear, and brake wear.

PAG was unable to supply VMT and other necessary activity data needed for the emission estimation process. Consequently, the needed information was obtained from the Arizona Department of Transportation (ADOT). The ADOT indicated that average daily VMT was 14.624 million miles per day. Seasonal adjustment factors had not been calculated for Pima County, so the adjustment factors calculated for Maricopa County were used. Like Maricopa County, this adjustment occurred in the motor vehicle temporal profiles. The ADOT divided average daily VMT into the 10 road classifications (urban and rural freeways, principal arterials, minor arterials, collectors, and local roads). Average vehicle speeds for each of these road types were assumed to be identical to Maricopa County.

4.1.3 Emission Calculation Method for Pinal and Gila Counties

Because detailed model parameters and transportation information were unavailable for Pinal and Gila Counties, motor vehicle emissions for these two counties were estimated in a much more simple and straightforward manner. Annual total VOC and PM_{10} emissions were taken from the existing GCVTC inventory database. These annual emissions were then divided by four to give emissions for each of the four seasons. These seasonal emissions were then adjusted for seasonal differences in VMT using the same seasonal adjustment procedure used for Maricopa and Pima Counties.

4.2 Motor Vehicle Data Development

Table 4-3 summarizes the different sources of data that were discussed in the motor vehicle emission calculation methods (Section 4.1). References and contacts for these data are also provided.

Table 4-3

Arizona HAPs On-Road Motor Vehicle Data Sources

Type of Data Needed		Reference
Existing VOC/PM Emissions	Existing emission estimates for Pinal and Gila Counties	GCVTC emissions inventory
Emission Factor Model Input Parameters	MOBILE5a and PART5 emission factor model input parameters for Maricopa County	Personal communication with Ms. Cari Anderson of MAGTPO, 12 April 1995
	MOBILE5a and PART5 emission factor model input parameters for Maricopa and Pima Counties	Personal communication with Ms. Lee Comrie of PAG, 5 May 1995
Emission Factors	VOC emission factors for Maricopa and Pima Counties	U.S. EPA, MOBILE5a emission factor model
	PM emission factors for Maricopa and Pima Counties	U.S. EPA, PART5 emission factor model
Activity Data	Vehicle miles traveled for Maricopa County	Personal communication with Ms. Cathy Arthur of MAGTPO, 8 May 1995
	Vehicle miles traveled for Pima County	Personal communication with Mr. M. Catchpole of ADOT, 8 May 1995
Speciation Profiles	VOC and PM speciation profiles for gasoline on-road motor vehicles	Desert Research Institute speciation profiles developed for Phoenix
	VOC and PM speciation profiles for diesel on-road motor vehicles	Desert Research Institute speciation profiles developed for Phoenix

5.0 DEVELOPMENT OF MODELING INVENTORIES

Modeling inventories have been prepared for use in air quality modeling and data analysis activities as part of the Arizona HAPs research program. A higher level of spatial and temporal resolution is provided in the modeling inventories than with the county-wide emission estimates. The modeling inventories consist of gridded, hourly HAP emission estimates. This section provides a brief overview of the development and results of the modeling inventories.

5.1 Spatial Allocation of Emissions

Emission estimates for area sources (including on-road motor vehicles) were initially generated at the county level. For gridded modeling applications, a more refined source description was produced. Sources were resolved for a 4000 meter by 4000 meter grid system using a universal transverse Mercator (UTM) map projection. County-level area sources were apportioned to individual grid cells by percentage of one of the following categories or spatial surrogates:

- County area;
- Population;
- Households;
- Urban area;
- Rural area;
- Wildfire or prescribed burn area;
- Major road presence (highways);
- Agricultural area (Maricopa County only);

- Commercial airports (Maricopa County only); and
- Military airports (Maricopa County only).

For example, if 10% of the population of a county resides in one grid cell, that grid cell is allocated 10% of the emissions of source types with population surrogates. Ratios of the amount of a surrogate in a grid cell to the total amount of a surrogate in a county were developed using the Arc/Info® geographical information system (GIS).

Table 5-1 lists the spatial surrogate used for each area source type. Maricopa County emissions were generally assigned to the spatial surrogates developed for the ozone SIP modeling program (Douglas, et al., 1994). Data to develop the surrogates was obtained from the 1990 census (population and housing), ROADNET (major roads, from American Digital Cartography, Inc.), and the GCVTC inventory (wildfires and prescribed burns). The areas covered by fire were assumed to be squares with the centroid and size equal to the location and acreage, respectively, reported in the GCVTC inventory. Emissions from fires were then evenly distributed among the total area in a given county covered by fire.

Pesticide application data developed by the University of Arizona for this study included location in Section/Township/Range coordinates. These were converted to UTM coordinates and the emissions data for each application were assigned to the grid cell in which the UTM coordinates fell.

Point sources were assigned to the appropriate grid cell using the latitude and longitude coordinates supplied for the stack locations. The coordinates were converted to UTM coordinates for use in the emissions modeling software.

Table 5-1

Area Source Spatial Surrogates

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.*
2102002000	Industrial Bituminous/Subbituminous Coal	Urban	Urban
2102004000	Industrial Distillate Oil	Urban	Urban
2102006000	Industrial Natural Gas	Urban	Urban
2102006001	Industrial Combustion - Natural Gas Boilers	Urban	Urban
2102012000	Industrial Combustion - Waste Oil	Urban	Urban
2103004000	Commercial/Institutional Distillate Oil	Urban	Urban
2103006000	Commercial/Institutional Natural Gas	Urban	Urban
2103006001	Commercial/Institutional Combustion - Natural Gas Boilers	Urban	Urban
2103006002	Commercial/Institutional Combustion - Natural Gas IC Engines	Urban	Urban
2104004000	Residential Distillate Oil	Households	Households
2104006000	Residential Natural Gas	Households	Households
2104008000	Residential Wood	Households	Households
2201001000	Highway Vehicles Light Duty Gasoline Vehicles (LDGV)	Highways	Highways
2201060000	Highway Vehicles Light Duty Gasoline Trucks 1 & 2 (LDGT)	Highways	Highways
2201070000	Highway Vehicles Heavy Duty Gasoline Vehicles (HDGV)	Highways	Highways
2201080000	Mobile Source - Motorcycles	Highways	Highways
2230001000	Highway Vehicles Light Duty Diesel Vehicles (LDDV)	Highways	Highways
2230060000	Highway Vehicles Light Duty Diesel Trucks (LDDT)	Highways	Highways
2230070000	Highway Vehicles Heavy Duty Diesel Vehicles (HDDV)	Highways	Highways
2260000000	All Off-Highway Vehicle Gasoline, 2-Stroke	Rural	Rural
2260001000	Off-Highway Vehicle Gasoline, 2-Stroke Recreational Vehicles	Rural	Rural
2260002000	Off-Highway Vehicle Gasoline, 2-Stroke Construction Equipment	Urban	Urban
2260003000	Off-Highway Vehicle Gasoline, 2-Stroke Industrial Equipment	Urban	Urban

Table 5-1

(Continued)

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.[a]
2275050000	Aircraft General Aviation	County Area	County Area
2275900000	Aircraft Refueling	County Area	County Area
2282005000	Marine Vessels, Recreational Pleasure Craft, Gasoline 2-Stroke	County Area	County Area
2282010000	Marine Vessels, Recreational Pleasure Craft, Gasoline 4-Stroke	County Area	County Area
2282020000	Marine Vessels, Recreational Pleasure Craft, Diesel	County Area	County Area
2285002000	Railroads Diesel	County Area	County Area
2294000000	Paved Road Dust	Highways	Highways
2294005000	Paved Roads Interstate/Arterial	Highways	Highways
2294010000	Paved Roads All Other Public Paved Roads	Highways	Highways
2296000000	Unpaved Roads All Unpaved Roads	Rural	Rural
2309100010	Electroplating	Urban	Urban
2310000000	Oil & Gas Production: SIC 13 All Processes	Urban	Urban
2311000100	Industrial Processes - Construction Wind Erosion	Urban	Urban
2399000000	Industrial Processes: NEC Industrial Processes: NEC	Urban	Urban
2401001000	Surface Coating Architectural Coatings	Population	Population
2401005000	Surface Coating Auto Refinishing: SIC 7532	Urban	Urban
2401008000	Surface Coating Traffic Markings	Urban	Urban
2401010000	Surface Coating - Textile Products	Urban	Urban
2401015000	Solvent Utilization Surface Coating	Urban	Urban
2401020000	Surface Coating Wood Furniture: SIC 25	Urban	Urban
2401025000	Surface Coating Metal Furniture: SIC 25	Urban	Urban
2401030000	Surface Coating Paper: SIC 26	Urban	Urban
2401035000	Surface Coating - Plastic Products	Urban	Urban
2401040000	Surface Coating Metal Cans: SIC 341	Urban	Urban
2401045000	Surface Coating Metal Coils: SIC 3498	Urban	Urban

Table 5-1

(Continued)

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.[a]
2401050000	Surface Coating - Miscellaneous Finished Metals	Urban	Urban
2401055000	Surface Coating Machinery & Equipment: SIC 35	Urban	Urban
2401060000	Surface Coating Large Appliances: SIC 363	Urban	Urban
2401065000	Solvent Utilization Surface Coating	Urban	Urban
2401070000	Surface Coating Motor Vehicles: SIC 371	Urban	Urban
2401075000	Surface Coating Aircraft: SIC 372	County Area	County Area
2401080000	Surface Coating Marine: SIC 373	County Area	County Area
2401090000	Surface Coating Misc. Manufacturing	Urban	Urban
2401100000	Solvent Utilization Surface Coating	Urban	Urban
2401200000	Solvent Utilization Surface Coating	Urban	Urban
2401990000	All surface coating categories	Urban	Urban
2415000000	Degreasing - All Processes	Urban	Urban
2415105000	Solvent Utilization Degreasing	Urban	Urban
2415110000	Degreasing Primary Metal Industries (SIC 33): Open Top Degreasing	Urban	Urban
2415120000	Solvent Utilization Degreasing	Urban	Urban
2415125000	Degreasing Industrial Machinery & Equip. (SIC 35): Open Top Degreasing	Urban	Urban
2415130000	Degreasing Electronic & Other Elec. (SIC 36): Open Top Degreasing	Urban	Urban
2415135000	Solvent Utilization Degreasing	Urban	Urban
2415140000	Solvent Utilization Degreasing	Urban	Urban
2415145000	Solvent Utilization Degreasing	Urban	Urban
2415305000	Solvent Utilization Degreasing	Urban	Urban
2415310000	Degreasing Primary Metal Industries (SIC 33): Cold Cleaning	Urban	Urban
2415320000	Solvent Utilization Degreasing	Urban	Urban

Table 5-1

(Continued)

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.[a]
2415325000	Degreasing Industrial Machinery & Equip. (SIC 35): Cold Cleaning	Urban	Urban
2415330000	Degreasing Electronic & Other Elec. (SIC 36): Cold Cleaning	Urban	Urban
2415335000	Solvent Utilization Degreasing	Urban	Urban
2415340000	Solvent Utilization Degreasing	Urban	Urban
2415345000	Solvent Utilization Degreasing	Urban	Urban
2415355000	Solvent Utilization Degreasing	Urban	Urban
2415360000	Solvent Utilization Degreasing	Urban	Urban
2415365000	Degreasing Miscellaneous Repair Services (SIC 76): Cold Cleaning	Urban	Urban
2420000055	Dry Cleaning - All Processes - Perchloroethylene	Population	Population
2420000370	Dry Cleaning - All Processes - Special Naphthas	Population	Population
2420010055	Solvent Utilization Dry Cleaning	Population	Population
2420010370	Solvent Utilization Dry Cleaning	Population	Population
2420020055	Dry Cleaning Coin-operated Cleaners	Population	Population
2425000000	Graphic Arts All Processes	Urban	Urban
2430000000	Rubber/Plastics All Processes	Urban	Urban
2440000000	Solvent Use - Miscellaneous Industrial	Urban	Urban
2440020000	Solvent Utilization Adhesive (Industrial) Application	Urban	Urban
2461021000	Miscellaneous Non-Industrial: Commercial Cutback Asphalt	Population	Population
2461022000	Emulsified Asphalt	Population	Population
2461023000	Asphalt Roofing	Population	Population
2461800000	Solvent Utilization Pesticide Application: All Processes	Rural	Rural
2465000000	Solvent Use - Non-Industrial Consumer - All Processes	Population	Population
2465100000	Miscellaneous Non-Industrial: Consumer Personal Care Products	Population	Population

Table 5-1

(Continued)

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.[a]
2465200000	Miscellaneous Non-Industrial: Consumer Household Products	Population	Population
2465400000	Solvent Utilization Automotive Aftermarket Products	Population	Population
2465600000	Miscellaneous Non-Industrial: Consumer Adhesives and Sealants	Population	Population
2501050120	Storage & Transport Petroleum & Petroleum Product Storage	Urban	Urban
2501060050	Petroleum & Petroleum Product Storage Gasoline Service Stations	Population	Population
2501060100	Petroleum & Petroleum Product Storage Gasoline Service Stations	Population	Population
2501060201	Petroleum & Petroleum Product Storage Gasoline Service Stations	Population	Population
2501995180	Kerosene Storage Working Loss	Population	Population
2505000120	Petroleum Transport - Gasoline	Urban	Urban
2505000150	Petroleum Transport - Jet Naphtha	Urban	Urban
2505000900	Tank Cleaning - All Transport Types	Urban	Urban
2505030120	Gasoline Truck Transport	Urban	Urban
2510000000	Organic Chemical Storage Breathing Loss	Urban	Urban
2601010000	On-Site Incineration Industrial	Urban	Urban
2601020000	On-Site Incineration Commercial/Institutional	Urban	Urban
2601030000	On-Site Incineration Residential	Households	Households
2610000000	Open Burning - All Categories	Urban	Urban
2610010000	Open Burning Industrial	Urban	Urban
2610020000	Open Burning Commercial/Institutional	Urban	Urban
2610030000	Open Burning Residential	Households	Households
2620030000	Municipal Landfills	Population	Population
2630020000	Wastewater Treatment Public Owned	Population	Population

Table 5-1

(Continued)

Area Source Code	Description	Spatial Surrogate	
		Gila, Pima, and Pinal Co.	Maricopa Co.[a]
2640000000	TSDFs All TSDF Types	Urban	Urban
2660000000	Leaking Underground Storage Tanks	Urban	Urban
27	LDGV - Limited Access Roads	Highways	Highways
2730100000	Geogenic Wind Erosion	County Area	County Area
2730100001	Geogenic Wind Erosion	County Area	County Area
2801000003	Agricultural Tilling	Rural	Rural
2810001000	Forest Wildfires	Wildfire	Wildfire
2810030000	Other Combustion Structure Fires	Population	Population
2810050000	Motor Vehicle Fires	Population	Population
2810015000	Prescribed Burning	Wildfire	Wildfire
2820000000	Cooling Towers	Urban	Urban
2850000010	Hospital Sterilization Operations	Population	Population
31	MDGV - Limited Access Roads	Highways	Highways
35	HDGV - Limited Access Roads	Highways	Highways
40	MDDV - Limited Access Roads	Highways	Highways
56	Unpaved Airstrip LTOs	County Area	County Area
97	Minor Points - Oil Boilers	Urban	Urban
98	Minor Points - Gas Boilers	Urban	Urban
9999999998	Swimming Pools	Households	Households

[a] Maricopa County spatial surrogates were from the Urban Airhsed Model (UAM) study performed for the ozone SIP analysis. Exceptions to this were highway surrogates, which were not used in the UAM study.

5.2 Temporal Allocation of Emissions

Hourly emission estimates obtained from either local APCDs or the TRI database were assumed to have constant emission rates (i.e., 24 hours per day). Point source emission estimates from the GCVTC inventory were temporally disaggregated to create season-specific daily estimates using the operating schedules contained in the base emission files. These data originate from Arizona's AIRs files.

Temporal profiles used by the California Air Resources Board were applied to most of the area source categories. The miscellaneous source types were assigned a default profile, evenly distributing the emissions over each hour of the year. Pesticide application data included the date of application. The pesticide emissions data could therefore be directly assigned to a season. The emissions for a given season were then summed and averaged over the number of hours in a season. Wildfire and prescribed burn emission estimates were likewise assigned to seasons using the dates provides in the GCVTC inventory. Average hourly values in each season were then calculated.

6.0 ADEQ REFINEMENTS OF INVENTORY

In an effort to strengthen certain elements of the inventory, emissions estimates for several source categories and chemicals are being refined by ADEQ, in coordination with Radian. Information is being gathered with a special survey of chrome-plating facilities, because of the potential toxicity of hexavalent chromium. Additional emissions information is also being developed on sources and uses of chloroform, 1,4-dichlorobenzene, trichloroethylene, methylene chloride, 1,3-butadiene, and formaldehyde.

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APPENDIX D

Research HAP List

Arizona Research HAPs List

CAS Number	Name	Criterion[a]
75-07-0	ACETALDEHYDE	CAA
60-35-5	ACETAMIDE	CAA
64-19-7	ACETIC ACID	TLV
108-24-7	ACETIC ANHYDRIDE	TLV
67-64-1	ACETONE	RfC
75-05-8	ACETONITRILE	CAA
81-81-2	ACETONYLBENZYLHYDROXYCOUMARIN,3-,ALP	RfC
98-86-2	ACETOPHENONE	CAA
79-04-9	ACETYL CHLORIDE, CHLORO-	TLV
53-96-3	2-ACETYLAMINOFLUORENE	CAA
79-27-6	ACETYLENE TETRABROMIDE	TLV
50-78-2	ACETYLSALICYLIC ACID	TLV
107-02-8	ACROLEIN	CAA
79-06-1	ACRYLAMIDE	CAA
79-10-7	ACRYLIC ACID	CAA
107-13-1	ACRYLONITRILE	CAA
111-69-3	ADIPONITRILE	TLV
116-06-3	ALDICARB	RfC
309-00-2	ALDRIN	CAN
107-18-6	ALLYL ALCOHOL	RfC
107-05-1	ALLYL CHLORIDE	CAA
106-92-3	ALLYL GLYCIDYL ETHER	TLV
2179-59-1	ALLYL PROPYL DISULFIDE	TLV
7446-70-0	ALUMINUM CHLORIDE	TLV
20859-73-8	ALUMINUM PHOSPHIDE, (ALP)	RfC
92-67-1	4-AMINOBIPHENYL	CAA
504-29-0	AMINOPYRIDINE,2-	TLV
504-24-5	AMINOPYRIDINE,4-	Eff
61-82-5	AMITROLE	TLV
7664-41-7	AMMONIA	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
123-92-2	AMYL ACETATE,ISO-	TLV
628-63-7	AMYLACETATE,N-	TLV
626-38-0	AMYLACETATE,SEC-	TLV
62-53-3	ANILINE	CAA
103-69-5	ANILINE, N-ETHYL	Eff
90-04-0	O-ANISIDINE	CAA
29191-52-4	ANISIDINE (O,P ISOMERS)	TLV
104-94-9	ANISIDINE,P-	TLV
	ANTIMONY COMPOUNDS	CAA
140-57-8	ARAMITE	CAN
11097-69-1	AROCLOR 1254	TLV
	ARSENIC COMPOUNDS (INORGANIC INCLUDING ARSINE)	CAA
1332-21-4	ASBESTOS	CAA
8052-42-4	ASPHALT (PETROLEUM) FUMES	TLV
1912-24-9	ATRAZINE	TLV
2642-71-9	AZINPHOS (ETHYL GUTHION)	Eff
103-33-3	AZOBENZENE	CAN
7440-39-3	BARIUM	RfC
1304-28-5	BARIUM OXIDE	TLV
55-38-9	BAYTEX	TLV
17804-35-2	BENOMYL	TLV
98-87-3	BENZAL CHLORIDE	Eff
100-52-7	BENZALDEHYDE	RfC
71-43-2	BENZENE (INCLUDING BENZENE FROM GASOLINE)	CAA
108-98-5	BENZENETHIOL	TLV
92-87-5	BENZIDINE	CAA
65-85-0	BENZOIC ACID	RfC
100-47-0	BENZONITRILE	Eff
98-07-7	BENZOTRICHLORIDE	CAA

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
98-88-4	BENZOYL CHLORIDE	Eff
94-36-0	BENZOYL PEROXIDE	TLV
100-44-7	BENZYL CHLORIDE	CAA
	BERYLLIUM COMPOUNDS	CAA
57-57-8	BETA-PROPIOLACTONE	CAA
92-52-4	BIPHENYL	CAA
117-81-7	BIS (2-ETHYLHEXYL)PHTHALATE (DEHP)	CAA
542-88-1	BIS(CHLOROMETHYL)ETHER	CAA
1304-82-1	BISMUTH TELLURIDE	TLV
80-05-7	BISPHENOL A	RfC
7632-04-4	BORATES, TETRA, SODIUM SALT (ANHYDROUS)	TLV
11130-12-4	BORATES, TETRA, SODIUM SALT (PENTAHYDRAT	TLV
1303-96-4	BORATES, TETRA, SODIUM SALTS	TLV
7440-42-8	BORON	RfC
10294-34-5	BORON CHLORIDE, (BCL3)	Eff
10294-33-4	BORON TRIBROMIDE	TLV
7637-07-2	BORON TRIFLUORIDE	TLV
7726-95-6	BROMINE	TLV
7789-30-2	BROMINE PENTAFLUORIDE	TLV
74-97-5	BROMOCHLOROMETHANE	TLV
75-27-4	BROMODICHLOROMETHANE	CAN
75-25-2	BROMOFORM	CAA
106-99-0	1,3-BUTADIENE	CAA
109-79-5	BUTANETHIOL	TLV
71-36-3	N-BUTANOL	RfC
78-92-2	BUTANOL,2-	TLV
1338-23-4	BUTANONEPEROXIDE,2-	TLV
123-86-4	1-BUTYL ACETATE	TLV
85-68-7	BUTYL BENZYL PHTHALATE	RfC

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
105-46-4	BUTYLACETATE,SEC-	TLV
540-88-5	BUTYLACETATE,TERT-	TLV
141-32-2	BUTYLACRYLATE,N-	TLV
75-65-0	BUTYLALCOHOL,T-	TLV
109-73-9	BUTYLAMINE,N-	TLV
13952-84-6	BUTYLAMINE,SEC-	Eff
75-64-9	BUTYLAMINE,TERT-	Eff
109-69-3	BUTYLCHLORIDE,N-	Eff
2426-08-6	BUTYLGLYCIDYLETHER,N-	TLV
138-22-7	BUTYLLACTATE,N-	TLV
98-54-4	BUTYLPHENOL,4-TERT-	Eff
89-72-5	BUTYLPHENOL,O-SEC-	TLV
98-51-1	BUTYLTOLUENE,P-TERT-	TLV
107-92-6	N-BUTYRIC ACID	Eff
	CADMIUM COMPOUNDS	CAA
156-62-7	CALCIUM CYANAMIDE	CAA
7789-75-5	CALCIUM FLUORIDE	TLV
1305-62-0	CALCIUM HYDROXIDE	TLV
10124-37-5	CALCIUM NITRATE	Eff
1305-78-8	CALCIUM OXIDE	TLV
76-22-5	CAMPHOR	TLV
76-22-2	CAMPHOR,SYNTHETIC	TLV
105-60-2	CAPROLACTAM	CAA
2425-06-1	CAPTAFOL	RfC
133-06-2	CAPTAN	CAA
63-25-2	CARBARYL	CAA
1563-66-2	CARBOFURAN	RfC
1333-86-4	CARBON BLACK	TLV
75-15-0	CARBON DISULFIDE	CAA

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
558-13-4	CARBON TETRABROMIDE	TLV
56-23-5	CARBON TETRACHLORIDE	CAA
353-50-4	CARBONYL FLUORIDE	TLV
463-58-1	CARBONYL SULFIDE	CAA
120-80-9	CATECOL	CAA
21351-79-1	CESIUM HYDROXIDE	TLV
75-87-6	CHLORAL	RfC
133-90-4	CHLORAMBEN	CAA
57-74-9	CHLORDANE	CAA
55720-99-5	CHLORINATED DIPHENYL OXIDE	TLV
7782-50-5	CHLORINE	CAA
10049-04-4	CHLORINE DIOXIDE	TLV
7790-91-2	CHLORINE TRIFLUORIDE	TLV
107-20-0	CHLOROACETALDEHYDE	TLV
79-11-8	CHLOROACETIC ACID	CAA
532-27-4	2-CHLOROACETOPHENONE	CAA
108-42-9	CHLOROANILINE,M-	Eff
106-47-8	CHLOROANILINE,P-	RfC
108-90-7	CHLOROBENZENE	CAA
510-15-6	CHLOROBENZILATE	CAA
2698-41-1	CHLOROBENZYLIDENEMALONONITRILE,O-	TLV
107-07-3	CHLOROETHANOL,2-	TLV
67-66-3	CHLOROFORM	CAA
107-30-2	CHLOROMETHYL METHYL ETHER	CAA
100-00-5	CHLORONITROBENZENE,4-	TLV
600-25-9	CHLORONITROPROPANE,1-,1-	TLV
108-43-0	CHLOROPHENOL,M-	Eff
95-57-8	CHLOROPHENOL,O-	RfC
76-06-2	CHLOROPICRIN	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
126-99-8	CHLOROPRENE	CAA
2039-87-4	CHLOROSTYRENE,O-	TLV
1897-45-6	CHLOROTHALONIL	RfC
95-49-8	CHLOROTOLUENE,O-	RfC
95-74-9	CHLOROTOLUIDINE,3-,P-	Eff
2921-88-2	CHLORPYRIFOS	RfC
	CHROMIUM COMPOUNDS	CAA
	COAL DUST	TLV
8001-58-9	COAL TAR	CAN
8007-45-2	COAL TAR PITCH VOLATILES	CAN
	COBALT COMPOUNDS	CAA
	COKE OVEN EMISSIONS	CAA
7440-50-8	COPPER	TLV
1344-67-8	COPPER CHLORIDE	TLV
7758-89-6	COPPER CHLORIDE, (CUCL)	TLV
	COPPER COMPOUNDS	TLV
1317-39-1	COPPER OXIDE, (CU2O)	TLV
1317-38-0	COPPER OXIDE, (CUO)	TLV
	COTTON DUST	TLV
108-39-4	M-CRESOL	CAA
95-48-7	O-CRESOL	CAA
106-44-5	P-CRESOL	CAA
1319-77-3	CRESOLS/CRESYLIC ACID (ISOMERS AND MIXTURE)	CAA
14464-46-1	CRISTOBALITE (SI02)	TLV
123-73-9	CROTONALDEHYDE	TLV
299-86-5	CRUFOMATE	TLV
98-82-8	CUMENE	CAA
80-15-9	CUMENE HYDROPEROXIDE	Eff
420-04-2	CYANAMIDE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
	CYANIDE COMPOUNDS[c]	CAA
108-93-0	CYCLOHEXANOL	TLV
108-94-1	CYCLOHEXANONE	TLV
108-91-8	CYCLOHEXYLAMINE	RfC
121-82-4	CYCLONITE	RfC
542-92-7	CYCLOPENTADIENE	TLV
96-37-7	CYCLOPENTANE, METHYL-	Eff
13121-70-5	CYHEXATIN	TLV
94-75-7	2,4-D, SALTS AND ESTERS	CAA
75-99-0	DALAPON	RfC
764-41-0	DCB	Eff
72-54-8	DDD	CAN
72-55-9	DDE	CAA
50-29-3	DDT	CAN
17702-41-9	DECABORANE	TLV
8065-48-3	DEMETON	TLV
2238-07-5	DI-2,3-EPOXYPROPYL ETHER	TLV
117-84-0	DI-N-OCTYL PHTHALATE	Eff
123-42-2	DIACETONE ALCOHOL	TLV
124-09-4	DIAMINOHEXANE,1,6-	TLV
333-41-5	DIAZINON	TLV
334-88-3	DIAZOMETHANE	CAA
132-64-9	DIBENZOFURANS	CAA
19287-45-7	DIBORANE	TLV
300-76-5	DIBROM	TLV
96-12-8	1,2-DIBROMO-3-CHLOROPROPANE	CAA
126-72-7	DIBROMOPROPYLPHOSPHATE,TRIS,2,3-	Eff
102-81-8	DIBUTYLAMINOETHANOL,2-N-	TLV
2528-36-1	DIBUTYLPHENYL PHOSPHATE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
107-66-4	DIBUTYLPHOSPHATE	TLV
84-74-2	DIBUTYLPHTHALATE	CAA
7572-29-4	DICHLOROACETYLENE	TLV
95-50-1	1,2-DICHLOROBENZENE	RfC
106-46-7	1,4-DICHLOROBENZENE(P)	CAA
91-94-1	3,3-DICHLOROBENZIDINE	CAA
75-71-8	DICHLORODIFLUOROMETHANE	RfC
118-52-5	DICHLORODIMETHYLHYDANTOIN,1,3-,5,5-	TLV
156-59-2	1,2-DICHLOROETHENE	TLV
540-59-0	DICHLOROETHYLENE,1,2-,CIS-TRANS-	TLV
111-44-4	DICHLOROETHYL ETHER (BIS(2-CHLOROETHYL)ETHER)	CAA
75-43-4	DICHLOROMONOFLUOROMETHANE	TLV
594-72-9	DICHLORONITROETHANE,1,1-,1-	TLV
120-83-2	2,4-DICHLOROPHENOL	RfC
87-65-0	DICHLOROPHENOL,2,6-	Eff
96-23-1	DICHLOROPROPANOL,1,3-,2-	Eff
542-75-6	1,3-DICHLOROPROPENE	CAA
62-73-7	DICHLORVOS	CAA
141-66-2	DICROTOPHOS	TLV
77-73-6	DICYCLOPENTADIENE	TLV
60-57-1	DIELDRIN	CAN
111-42-2	DIETHANOLAMINE	CAA
121-69-7	N,N-DIETHYL ANILINE (N,N-DIMETHYLANILINE)	CAA
96-22-0	DIETHYL KETONE	TLV
84-66-2	DIETHYL PHTHALATE	RfC
64-67-5	DIETHYL SULFATE	CAA
109-89-7	DIETHYLAMINE	TLV
100-37-8	DIETHYLAMINOETHANOL,2-	TLV
111-40-0	DIETHYLENE TRIAMINE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
75-61-6	DIFLUORODIBROMOMETHANE	TLV
108-83-8	DIISOBUTYL KETONE	TLV
108-18-9	DIISOPROPYLAMINE	TLV
119-90-4	3,3-DIMETHOXYBENZIDINE	CAA
127-19-5	DIMETHYL ACETAMIDE	TLV
60-11-7	DIMETHYL AMINOAZOBENZENE	CAA
119-93-7	3,3'-DIMETHYL BENZIDINE	CAA
79-44-7	DIMETHYL CARBAMOYL CHLORIDE	CAA
624-92-0	DIMETHYL DISULFIDE	Eff
68-12-2	DIMETHYL FORMAMIDE	CAA
57-14-7	1,1-DIMETHYL HYDRAZINE	CAA
131-11-3	DIMETHYL PHTHALATE	CAA
77-78-1	DIMETHYL SULFATE	CAA
75-18-3	DIMETHYL SULFIDE	Eff
4685-14-7	DIMETHYL-4,4-BIPYRIDINIUM,1,1-	TLV
124-40-3	DIMETHYLAMINE	TLV
1300-73-8	DIMETHYLAMINOBENZENE,4-	TLV
540-73-8	DIMETHYLHYDRAZINE,1,2-	Eff
148-01-6	DINITOLMIDE	TLV
534-52-1	4,6-DINITRO-O-CRESOL, AND SALTS	CAA
99-65-0	DINITROBENZENE,1,3-	RfC
528-29-0	DINITROBENZENE,O	TLV
100-25-4	DINITROBENZENE,P	TLV
88-85-7	DINITROBUTYLPHENOL,2,4-,6-SEC-	RfC
51-28-5	2,4-DINITROPHENOL	CAA
25321-14-6	DINITROTOLUENE	TLV
121-14-2	2,4-DINITROTOLUENE	CAA
606-20-2	DINITROTOLUENE,2,6-	CAN
123-91-1	1,4-DIOXANE (1,4-DIETHYLENEOXIDE)	CAA

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
109-94-4	ETHYL FORMATE	TLV
97-63-2	ETHYL METHACRYLATE	Eff
106-93-4	ETHYLENE DIBROMIDE (DIBROMOETHANE)	CAA
107-06-2	ETHYLENE DICHLORIDE (1,2-DICHLOROETHANE)	CAA
107-21-1	ETHYLENE GLYCOL	CAA
628-96-6	ETHYLENE GLYCOL DINITRATE	TLV
151-56-4	ETHYLENE IMINE (AZIRIDINE)	CAA
96-45-7	ETHYLENE THIOUREA	CAA
107-15-3	ETHYLENEDIAMINE	RfC
75-34-3	ETHYLIDENE DICHLORIDE (1,1-DICHLOROETHANE)	CAA
16219-75-3	ETHYLIDENE-2-NORBORNENE	TLV
100-74-3	ETHYLMORPHOLINE,N-	TLV
115-90-2	FENSULFOTHION	TLV
12604-58-9	FERROVANADIUM DUST	TLV
	FINE MINERAL FIBERS[d]	CAA
16984-48-8	FLUORIDES	TLV
7782-41-4	FLUORINE	RfC
62-74-8	FLUOROACETIC ACID SODIUM SALT	TLV
944-22-9	FONOFOS	TLV
50-00-0	FORMALDEHYDE	CAA
75-12-7	FORMAMIDE	TLV
64-18-6	FORMIC ACID	TLV
98-01-1	FURFURAL	RfC
98-00-0	FURFURAL ALCOHOL	TLV
961-11-5	GARDONA	RfC
7782-65-2	GERMANIUM TETRAHYDRIDE	TLV
111-30-8	GLUTARALDEHYDE	TLV
765-34-4	GLYCIDALDEHYDE	RfC
556-52-5	GLYCIDOL	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
	GLYCOL ETHERS[e]	CAA
	GRAIN DUST	TLV
7782-42-5	GRAPHITE	TLV
86-50-0	GUSATHION	TLV
151-67-7	HALOTHANE	TLV
76-44-8	HEPTACHLOR	CAA
1024-57-3	HEPTACHLOR EPOXIDE	CAN
110-43-0	2-HEPTANONE	TLV
123-19-3	HEPTANONE,4-	TLV
118-74-1	HEXACHLOROBENZENE	CAA
87-68-3	HEXACHLOROBUTADIENE	CAA
608-73-1	HEXACHLOROCYCLOHEXANE	CAN
77-47-4	HEXACHLOROCYCLOPENTADIENE	CAA
67-72-1	HEXACHLOROETHANE	CAA
70-30-4	HEXACHLOROPHENE	RfC
684-16-2	HEXAFLUOROACETONE	TLV
822-06-0	HEXAMETHYLENE-1,6-DIISOCYANATE	CAA
680-31-9	HEXAMETHYLPHOSPHORAMIDE	CAA
110-54-3	HEXANE	CAA
591-78-6	HEXANONE,2-	TLV
108-84-9	HEXYL ACETATE,SEC-	TLV
107-41-5	HEXYLENE GLYCOL	TLV
302-01-2	HYDRAZINE	CAA
7782-79-8	HYDRAZOIC ACID	Eff
10034-85-2	HYDRIODIC ACID	Eff
7647-01-0	HYDROCHLORIC ACID (HYDROGEN CHLORIDE (GAS ONLY))	CAA
10035-10-6	HYDROGEN BROMIDE	TLV
7664-39-3	HYDROGEN FLUORIDE (HYDROFLUORIC ACID)	CAA
7722-84-1	HYDROGEN PEROXIDE (30%)	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
7783-06-4	HYDROGEN SULFIDE	RfC
123-31-9	HYDROQUINONE	CAA
150-76-5	HYDROQUINONE MONOMETHYL ETHER	TLV
999-61-1	HYDROXYPROPYLACRYLATE,2-	TLV
95-13-6	INDENE	TLV
7440-74-6	INDIUM	TLV
7553-56-2	IODINE	TLV
75-47-8	IODOFORM	TLV
7758-94-3	IRON (II) CHLORIDE	TLV
1317-61-9	IRON (II,III) OXIDE	TLV
1309-37-1	IRON (III) OXIDE	TLV
	IRON (SOLUBLE COMPOUNDS)	TLV
13463-40-6	IRON PENTACARBONYL	TLV
123-51-3	ISOAMYL ALCOHOL	TLV
110-19-0	ISOBUTYL ACETATE	TLV
78-83-1	ISOBUTYL ALCOHOL	RfC
78-84-2	ISOBUTYRALDEHYDE	Eff
78-82-0	ISOBUTYRONITRILE	Eff
26952-21-6	ISOOCTYL ALCOHOL	TLV
78-59-1	ISOPHORONE	CAA
4098-71-9	ISOPHORONE DIISOCYANATE	TLV
4016-14-2	ISOPROPYL GLYCIDYL ETHER	TLV
768-52-5	ISOPROPYLANILINE,N-	TLV
1332-58-7	KAOLIN	TLV
143-50-0	KEPONE	Eff
463-51-4	KETENE	TLV
54-11-5	L-NICOTINE	TLV
	LEAD COMPOUNDS	CAA
64742-95-6	LIGHT AROMATIC SOLVENT NAPTHA	CAN

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
58-89-9	LINDANE	CAA
7580-67-8	LITHIUM HYDRIDE	TLV
7783-40-6	MAGNESIUM FLUORIDE	TLV
121-75-5	MALATHION	RfC
110-16-7	MALEIC ACID	Eff
10-83-1	MALEIC ANHYDRIDE	CAA
108-31-6	MALEIC ANHYDRIDE	RfC
109-77-3	MALONONITRILE	Eff
	MANGANESE COMPOUNDS	CAA
108-78-1	MELAMINE	Eff
	MERCURY COMPOUNDS	CAA
141-79-7	MESITYL OXIDE	TLV
79-41-4	METHACRYLIC ACID	TLV
126-98-7	METHACRYLONITRILE	RfC
74-93-1	METHANETHIOL	TLV
67-56-1	METHANOL	CAA
16752-77-5	METHOMYL	RfC
72-43-5	METHOXYCHLOR	CAA
79-20-9	METHYL ACETATE	TLV
96-33-3	METHYL ACRYLATE	TLV
74-83-9	METHYL BROMIDE (BROMOMETHANE)	CAA
74-87-3	METHYL CHLORIDE (CHLOROMETHANE)	CAA
71-55-6	METHYL CHLOROFORM (1,1,1-TRICHLOROETHANE)	CAA
8022-00-2	METHYL DEMETON	TLV
78-93-3	METHYL ETHYL KETONE (2-BUTANONE)	CAA
107-31-3	METHYL FORMATE	TLV
60-34-4	METHYL HYDRAZINE	CAA
74-88-4	METHYL IODIDE (IODOMETHANE)	CAA
110-12-3	METHYL ISOAMYL KETONE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
108-10-1	METHYL ISOBUTYL KETONE (HEXONE)	CAA
624-83-9	METHYL ISOCYANATE	CAA
563-80-4	METHYL ISOPROPYL KETONE	TLV
80-62-6	METHYL METHACRYLATE	CAA
298-00-0	METHYL PARATHION	RfC
107-87-9	N-METHYL PROPYL KETONE	TLV
98-83-9	METHYL STYRENE	TLV
1634-04-4	METHYL TERT BUTYL ETHER	CAA
79-84-4	METHYL VINYL KETONE	Eff
137-05-3	METHYL-2-CYANOACRYLATE	TLV
100-61-8	METHYLANILINE,N-	TLV
25639-42-3	METHYLCYCLOHEXANOL	TLV
583-60-8	METHYLCYCLOHEXANONE,0-	TLV
5124-30-1	METHYLENE BIS(4-CYCLOHEXYLISOCYANATE)	TLV
75-09-2	METHYLENE CHLORIDE (DICHLOROMETHANE)	CAA
101-68-8	METHYLENE DIPHENYL DIISOCYANATE (MDI)	CAA
101-14-4	4,4'-METHYLENEBIS(2-CHLOROANILINE)	CAA
101-77-9	4,4-METHYLENEDIANILINE	CAA
108-11-2	METHYLISOBUTYLCARBINOL	TLV
21087-64-9	METRIBUZIN	RfC
7786-34-7	MEVINPHOS	TLV
12001-26-2	MICA, RESPIRABLE	TLV
2385-85-5	MIREX	CAN
7439-98-7	MOLYBDENUM	RfC
	SOLUBLE MOLYBDENUM COMPOUNDS	TLV
6923-22-4	MONOCROTOPHOS	TLV
75-04-7	MONOETHYLAMINE	TLV
75-31-0	MONOISOPROPYLAMINE	TLV
74-89-5	MONOMETHYLAMINE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
110-91-8	MORPHOLINE	TLV
91-20-3	NAPHTHALENE	CAA
86-88-4	NAPHTHYLTHIOUREA,1-,1-,2-	TLV
	NICKEL COMPOUNDS	CAA
7697-37-2	NITRIC ACID	TLV
139-13-9	NITRILOTRIACETIC ACID	Eff
100-01-6	NITROANILINE,P-	TLV
99-59-2	NITROANISIDINE,5-,O-	Eff
92-93-3	4-NITROBIPHENYL	CAA
79-24-3	NITROETHANE	TLV
1836-75-5	NITROFEN	Eff
7783-54-2	NITROGEN TRIFLUORIDE	TLV
55-63-0	NITROGLYCERINE	TLV
75-52-5	NITROMETHANE	TLV
100-02-7	4-NITROPHENOL	CAA
79-46-9	2-NITROPROPANE	CAA
108-03-2	NITROPROPANE,1-	TLV
924-16-3	N-NITROSO-DI-N-BUTYLAMINE	CAN
684-93-5	N-NITROSO-N-METHYLUREA	CAA
98-95-3	NITROSOBENZENE	CAA
55-18-5	N-NITROSODIETHYLAMINE	CAN
62-75-9	N-NITROSODIMETHYLAMINE	CAA
59-89-2	N-NITROSOMORPHOLINE	CAA
930-55-2	N-NITROSOPYRROLIDINE	CAN
1321-12-6	NITROTOLUENE	TLV
99-08-1	NITROTOLUENE, M-	TLV
88-72-2	NITROTOLUENE,O-	TLV
99-99-0	NITROTOLUENE,P-	TLV
10024-97-2	NITROUS OXIDE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
111-84-2	NONANE,N-	TLV
3825-26-1	OCTANOIC ACID, PENTADECAFLUORO-, AMMONIU	TLV
8012-95-1	OIL MIST, MINERAL	TLV
	ORGANIC TIN COMPOUNDS	TLV
20816-12-0	OSMIUM TETROXIDE	TLV
144-62-7	OXALIC ACID (ANHYDROUS)	TLV
7783-41-7	OXYGEN DIFLUORIDE	TLV
8002-74-2	PARAFFIN WAX FUME	TLV
1910-42-5	PARAQUAT	TLV
56-38-2	PARATHION	CAA
19624-22-7	PENTABORANE	TLV
608-93-5	PENTACHLOROBENZENE	RfC
76-01-7	PENTACHLOROETHANE	Eff
82-68-8	PENTACHLORONITROBENZENE	CAA
87-86-5	PENTACHLOROPHENOL	CAA
110-62-3	PENTANAL	TLV
594-42-3	PERCHLOROMETHYL MERCAPTAN	TLV
7616-94-6	PERCHLORYL FLUORIDE	TLV
382-21-8	PERFLUOROISOBUTYLENE	TLV
22224-92-6	PHENAMIPHOS	TLV
108-95-2	PHENOL	CAA
92-84-2	PHENOTHIAZINE	TLV
638-21-1	PHENYL PHOSPHINE	TLV
106-50-3	P-PHENYLENEDIAMINE	CAA
108-45-2	PHENYLENEDIAMINE,M-	RfC
95-54-5	PHENYLENEDIAMINE,O-	TLV
100-63-0	PHENYLHYDRAZINE	TLV
298-02-2	PHORATE	TLV
75-44-5	PHOSGENE	CAA

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
732-11-6	PHOSMET	Eff
13171-21-6	PHOSPHAMIDON	Eff
7803-51-2	PHOSPHINE	CAA
7664-38-2	PHOSPHORIC ACID	TLV
10025-87-3	PHOSPHOROUS OXYCHLORIDE	TLV
10026-13-8	PHOSPHOROUS PENTACHLORIDE	TLV
7647-19-0	PHOSPHOROUS PENTAFLUORIDE	TLV
1314-80-3	PHOSPHOROUS PENTASULFIDE	TLV
7723-14-0	PHOSPHORUS	CAA
7719-12-2	PHOSPHORUS TRICHLORIDE	TLV
85-44-9	PHTHALIC ANHYDRIDE	CAA
626-17-5	PHTHALODINITRILE,M-	TLV
108-99-6	PICOLINE,BETA-	Eff
88-89-1	PICRIC ACID	TLV
142-64-3	PIPERAZINE DIHYDROCHLORIDE	TLV
83-26-1	PIVALYLINDANDIONE,2-,1,3-	TLV
7440-06-4	PLATINUM	TLV
	SOLUBLE PLATINUM SALTS	TLV
1336-36-3	POLYCHLORINATED BIPHENYLS (AROCLORS)	CAA
	POLYCYCLIC ORGANIC MATTER[f]	CAA
7440-09-7	POTASSIUM	Eff
7789-23-3	POTASSIUM FLUORIDE	TLV
7789-29-9	POTASSIUM FLUORIDE, (K(HF2))	TLV
1310-58-3	POTASSIUM HYDROXIDE	TLV
23950-58-5	PRONAMIDE	RfC
1120-71-4	1,3-PROPANE SULTONE	CAA
57-55-6	PROPANEDIOL,1,2-	RfC
71-23-8	N-PROPANOL	TLV
78-95-5	2-PROPANONE, 1-CHLORO-	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
107-19-7	PROPARGYL ALCOHOL	TLV
123-38-6	PROPIONALDEHYDE	CAA
79-09-4	PROPIONIC ACID	TLV
598-78-7	PROPIONIC ACID, 2-CHLORO-	TLV
107-12-0	PROPIONITRILE	Eff
114-26-1	PROPOXUR (BAYGON)	CAA
109-60-4	N-PROPYL ACETATE	TLV
78-87-5	PROPYLENE DICHLORIDE (1,2-DICHLOROPROPANE)	CAA
6423-43-4	PROPYLENE GLYCOL DINITRATE	TLV
75-56-9	PROPYLENE OXIDE	CAA
75-55-8	1,2-PROPYLENIMINE (2-METHYL AZIRIDINE)	CAA
627-13-4	PROPYLNITRATE,N-	TLV
8003-34-7	PYRETHRUM	TLV
110-86-1	PYRIDINE	RfC
14808-60-7	QUARTZ (SILICA DUST)	TLV
91-22-5	QUINOLINE	CAA
106-51-4	QUINONE	CAA
	RADIONUCLIDES (INCLUDING RADON)[g]	CAA
50-55-5	RESERPINE	Eff
55-55-5	RESERPINE	Eff
108-46-3	RESORCINOL	TLV
	SOLUBLE RHODIUM COMPOUNDS	TLV
	INSOLUBLE RHODIUM COMPOUNDS	TLV
7440-16-6	RHODIUM METAL, FUME AND DUST, AS RH	TLV
	ROSIN CORE SOLDER PYROLYSIS PRODUCTS	TLV
	ROSIN VAPORS	TLV
83-79-4	ROTENONE	TLV
	SELENIUM COMPOUNDS	CAA
7803-62-5	SILANE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
69012-64-2	SILICA, FUME	TLV
60676-86-0	SILICA VITREOUS	TLV
78-10-4	SILICIC ACID, TETRAETHYL ESTER	TLV
681-84-5	SILICIC ACID, TETRAMETHYL ESTER	TLV
7440-22-4	SILVER	RfC
	SOLUBLE SILVER COMPOUNDS	TLV
26628-22-8	SODIUM AZIDE	TLV
7631-90-5	SODIUM BISULFITE	TLV
7681-49-4	SODIUM FLUORIDE	TLV
1310-73-2	SODIUM HYDROXIDE	TLV
7681-57-4	SODIUM METABISULFITE	TLV
8052-41-3	STODDARD SOLVENT	TLV
7440-24-6	STRONTIUM	RfC
57-24-9	STRYCHNINE	RfC
100-42-5	STYRENE	CAA
96-09-3	STYRENE OXIDE	CAA
1395-21-7	SUBTILISINS	TLV
7704-34-9	SULFUR	Eff
10025-67-9	SULFUR MONOCHLORIDE	TLV
5714-22-7	SULFUR PENTAFLUORIDE	TLV
7783-60-0	SULFUR TETRAFLUORIDE	TLV
7446-11-9	SULFUR TRIOXIDE	Eff
7664-93-9	SULFURIC ACID	TLV
2699-79-8	SULFURYL FLUORIDE	TLV
35400-43-2	SULPROFOS	TLV
14807-96-6	TALC	TLV
7440-25-7	TANTALUM	TLV
7783-80-4	TELLERIUM HEXAFLUORIDE, AS TE	TLV
13494-80-9	TELLURIUM AND COMPOUNDS, AS TE	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
107-49-3	TEPP	TLV
100-21-0	TEREPHTHALIC ACID	Eff
26140-60-3	TERPHENYL	TLV
61788-32-7	TERPHENYL, HYDROGENATED	TLV
92-94-4	TERPHENYLS	TLV
95-94-3	1,2,4,5-TETRACHLOROBENZENE	RfC
1746-01-6	2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN	CAA
79-34-5	1,1,2,2-TETRACHLOROETHANE	CAA
127-18-4	TETRACHLOROETHYLENE (PERCHLOROETHYLENE)	CAA
58-90-2	2,3,4,6-TETRACHLOROPHENOL (2,4,5,6)	RfC
3689-24-5	TETRAETHYL DITHIOPYROPHOSPHATE	RfC
112-57-2	TETRAETHYLENEPENTAMINE	Eff
97-77-8	TETRAETHYLTHIURAM DISULFIDE	TLV
109-99-9	TETRAHYDROFURAN	TLV
3333-52-6	TETRAMETHYLSUCCINONITRILE	TLV
509-14-8	TETRANITROMETHANE	TLV
7722-88-5	TETRASODIUM PYROPHOSPHATE	TLV
479-45-8	TETRYLTRINITROPHENYLMETHYLNITRAMINE,2,4,	TLV
7440-28-0	THALLIUM	TLV
563-68-8	THALLIUM (I) ACETATE	RfC
6533-73-9	THALLIUM (I) CARBONATE	RfC
7791-12-0	THALLIUM (I) CHLORIDE	RfC
10102-45-1	THALLIUM (I) NITRATE	RfC
7446-18-6	THALLIUM (I) SULFATE	RfC
68-11-1	THIOGLYCOLIC ACID	TLV
7719-09-7	THIONYL CHLORIDE	TLV
62-56-6	THIOUREA	Eff
137-26-8	THIRAM	RfC
	INORGANIC TIN AND OXIDE COMPOUNDS	TLV

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
7440-31-5	TIN, AS SN	TLV
7550-45-0	TITANIUM TETRACHLORIDE	CAA
108-88-3	TOLUENE	CAA
95-80-7	2,4-TOLUENE DIAMINE	CAA
584-84-9	2,4-TOLUENE DIISOCYANATE	CAA
95-53-4	O-TOLUIDINE	CAA
108-44-1	TOLUIDINE,M-	TLV
106-49-0	TOLUIDINE,P-	TLV
8001-35-2	TOXAPHENE (CHLORINATED CAMPHENE)	CAA
126-73-8	TRIBUTYL PHOSPHATE	TLV
688-73-3	TRIBUTYL TIN	TLV
76-03-9	TRICHLOROACETIC ACID	TLV
120-82-1	1,2,4-TRICHLOROBENZENE	CAA
79-00-5	1,1,2-TRICHLOROETHANE	CAA
79-01-6	TRICHLOROETHYLENE	CAA
95-95-4	2,4,5-TRICHLOROPHENOL	CAA
88-06-2	2,4,6-TRICHLOROPHENOL	CAA
93-76-5	TRICHLOROPHENOXYACETIC ACID,2,4,5-	RfC
96-18-4	TRICHLOROPROPANE,1,2,3-	RfC
78-30-8	TRICRESYLPHOSPHATE,O-	TLV
15468-32-3	TRIDYIMITE	TLV
121-44-8	TRIETHYLAMINE	CAA
1582-09-8	TRIFLURALIN	CAA
552-30-7	TRIMELLITIC ANHYDRIDE	TLV
121-45-9	TRIMETHYL PHOSPHITE	TLV
75-50-3	TRIMETHYLAMINE	TLV
25551-13-7	TRIMETHYLBENZENE	TLV
540-84-1	2,2,4-TRIMETHYLPENTANE	CAA
118-96-7	TRINITROTOLUENE,2,4,6-	RfC

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
110-88-3	TRIOXANE,1,3,5-	Eff
115-86-6	TRIPHENYL PHOSPHATE	TLV
603-34-9	TRIPHENYLAMINE	TLV
76-87-9	TRIPHENYLTIN HYDROXIDE	TLV
1317-95-9	TRIPOLI	TLV
7440-33-7	TUNGSTEN AND COMPOUNDS, AS W	TLV
	INSOLUBLE TUNGSTEN COMPOUNDS	TLV
	SOLUBLE TUNGSTEN COMPOUNDS	TLV
1314-35-8	TUNGSTEN OXIDE, (WO3)	TLV
8006-64-2	TURPENTINE	TLV
57-13-6	UREA	Eff
1314-62-1	VANADIUM PENTOXIDE	RfC
108-05-4	VINYL ACETATE	CAA
593-60-2	VINYL BROMIDE	CAA
75-01-4	VINYL CHLORIDE	CAA
75-02-5	VINYL FLUORIDE	Eff
25013-15-4	VINYL TOLUENE	TLV
100-40-3	VINYLCYCLOHEXENE,4-	TLV
106-87-6	VINYLCYCLOHEXENEDIOXIDE,1-,3-	TLV
75-35-4	VINYLIDENE CHLORIDE (DICHLOROETHYLENE)	CAA
75-38-7	VINYLIDENE FLUORIDE	Eff
	WELDING FUMES	TLV
	WOOD DUST	TLV
1477-55-0	XYLENEDIAMINE,M-,A,A'-	TLV
106-42-3	P-XYLENES	CAA
95-47-6	O-XYLENES	CAA
108-38-3	M-XYLENES	CAA
1330-20-7	XYLENES (ISOMERS & MIXTURE)	CAA
1300-71-6	XYLENOL	Eff

Arizona Research HAPS List (cont)

CAS Number	Name	Criterion[a]
7440-65-5	YTTRIUM	TLV
7440-66-6	ZINC	RfC
7699-45-8	ZINC BROMIDE	Eff
7646-85-7	ZINC CHLORIDE	TLV
1314-13-2	ZINC OXIDE FUME	TLV
1314-84-7	ZINC PHOSPHIDE	RfC
7440-67-7	ZIRCONIUM	TLV
1314-23-4	ZIRCONIUM OXIDE	TLV

Notes:

[a] Criterion for inclusion in list:

CAA: Listed in Section 112(b) of Clean Air Act Amendments of 1990
CAN: Known or suspeceted human carcinogen
RfC: Reference concentration or reference dose has been established by U.S. EPA and is listed in IRIS
TLV: Time-weighted average ACGIH threshold limit value (TLV) is less than 200 parts-per-million volume or 5 milligrams per cubic meter
Eff: Human health effects are reported in M. Sittig, "Handbook of Toxic and Hazardous Chemicals and Carcinogens," Third Edition, New Jersey, Noyes Publications (1991), but none of the previous criteria applies and a TLV has not been adopted

The first criterion that applies is listed.

[b] For all listings above which contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e. antimony , arsenic, etc.) as part of that chemical's infrastructure.

[c] X'CN where X' = H or any other group where a formal dissociation may occur. For example KCN or $Ca(CN)_2$

[d] includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

[e] includes mono- and di- ethers of ethylene glycol, diethylene glycol, and triethylene glycol
$R-(OCH2CH2)_n-OR'$ where
n = 1, 2, or 3
R = alkyl or aryl groups
R' = R, H, or groups which, when removed, yield glycol ethers with structure:

R-(OCH2CH)$_n$-OH;
polymers are excluded from the glycol category.

[f] includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C

[g] a type of atom which spontaneously undergoes radioactive decay.

APPENDIX E

Description of Air Quality Simulation Model

Air Quality Simulation Model

The basis of the air quality model is the mass conservation equation for the mixing ratio, q, for each species

$$\frac{Dq}{Dt} = \frac{\partial q}{\partial t} + u_i \frac{\partial q}{\partial x_i} = \frac{1}{\rho_a}\frac{\partial}{\partial x_i}\left(\rho_a K_i \frac{\partial q}{\partial x_i}\right) + \frac{(S+R)}{\rho_a} \qquad (1)$$

where

$$q = \frac{C}{\rho_a}$$

In Equation (1), K is the turbulent eddy diffusivity, S is a source (emissions) term, R is a removal term, ρ_a is the density of air, C is the concentration of the species, and u_i represents the mean velocities in the three co-ordinate directions $i = x,y,z$; x and y are the east-west and north-south coordinates, and z is measured in the vertical direction. Note that the mass conservation equation is written in terms of the dimensionless mixing ratio, q, rather that the concentration, C, which has the units of mass/volume.

The left hand side of Equation (1) represents the total derivative of q along the trajectory described by the velocity field, u_i. This representation allows us to solve the equation using the semi-Lagrangian advection scheme (Smolarkiewicz and Pudykiewicz, 1992).

The air quality model solves the mass conservation equation on a Universal Transverse Mercator (UTM) fixed grid system with regular spacing in the horizontal and non-uniform spacing in the vertical. For example, the grid system for Phoenix consists of 6 vertical layers and 32 by 24 grid cells per layer. The size of each grid cell is 6 km on each side. The top of the modeling domain is at 4 km, and the spacing of the vertical layers is non-uniform to allow finer resolution near the surface, where the largest vertical gradients of important variables such as concentrations, turbulence, and winds occur. Four of the six vertical layers are within 1 km of the ground.

The air quality model is based on the regional Acid Deposition and Oxident Model (ADOM), which is described elsewhere (Venkatram et al., 1988). In the following sections, we confine our attention to processes that were modified in ADOM to develop the model for the Arizona HAPs research application. The gridded, three-dimensional wind, temperature and relative humidity

fields required by the air quality model are provided by a diagnostic meteorological model described in the following section.

Diagnostic Meteorological Model

The diagnostic meteorological model generates a three-dimensional mass-consistent wind field based on available wind data. This is achieved in two steps. In the first step, the surface and upper air data are horizontally and vertically interpolated throughout the domain of interest to generate gridded x- and y- components of the wind field. In the second step, using variational calculus, minimal adjustments are made to the interpolated wind field in order to eliminate divergence.

The horizontal interpolation scheme used by the diagnostic model is the inverse-distance-squared (IDS) method suggested by Ross et al. (1987). In the vertical, the model linearly interpolates the velocities vertically to the grid heights. If desired, a cubic spline interpolation technique can be used instead of linear interpolation. The velocities at each grid height are then linearly interpolated in time to obtain data at each model time step. The IDS method is used next to interpolate the upper-air velocities at each model time step and at each grid level horizontally to the grid cell centers.

Once the interpolation is complete, it is necessary to adjust the interpolated velocity field for mass consistency. This is accomplished by defining an integral function whose optimum solution minimizes the variance of the difference between the given and the adjusted velocity components. The integral function is solved under the constraint that the solution must satisfy the continuity equation. The integral function is defined in the weighted least-squares sense and the Lagrangian multiplier is used to incorporate the continuity constraint within it as follows:

$$F(U,V,W,\lambda) = \iiint_V \{\alpha_1^2(U-U_o)^2 + \alpha_1^2(V-V_o)^2 + \alpha_2^2(W-W_o)^2 + \lambda(\nabla\cdot V)\}\, dxdyd\rho \quad (2)$$

where

$$\nabla\cdot V = \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} + \frac{\partial W}{\partial \rho}, \quad (3)$$

and U_o, V_o, W_o, are the observed wind velocity components; U, V and W are the adjusted wind velocity components; λ (x,y,ρ) is the Lagrangain multiplier; and α_1 and α_2 are the weights

associated with the horizontal and vertical components, respectively. All the velocity components are in terrain-following coordinate system (x, y, ρ).

The solution of the integral equation leads to the following differential equation for the Lagrangian multiplier, λ.

$$\frac{\partial^2\lambda}{\partial x^2} + \frac{\partial^2\lambda}{\partial y^2} + \left(\frac{\alpha_1}{\alpha_2}\right)\frac{\partial^2\lambda}{\partial \rho^2} = -2\alpha_1^2\left(\frac{\partial U_o}{\partial x} + \frac{\partial V_o}{\partial y} + \frac{\partial W_o}{\partial \rho}\right) \qquad (4)$$

with the following boundary conditions:

$$\frac{\partial\lambda}{\partial\rho} = 0 \textit{ at the terrain surface}$$

$$\lambda = 0 \textit{ at the terrain boundaries}$$

The model uses a Successive-Over-Relaxation (SOR) method to solve the Poisson Equation (4).

The diagnostic meteorological model also interpolates the available surface and upper air temperature and relative humidity data to generate hourly, three-dimensional gridded fields of temperature and relative humidity. The daytime and nocturnal boundary layer parameters, viz., the micrometeorological surface scaling variables and the mixing heights, as well as vertical diffusivities are also provided to the air quality model by the diagnostic meteorological model. The vertical diffusivity (K_z in Equation 1) parameterization in the model follows Venkatram (1980) and Brost and Wyngaard (1978). The daytime and nocturnal micrometeorological varaibles are calculated as described in Venkatram (1980) and Dyer (1974).

Selection of Modeling Domain and Grid System

The atmospheric modeling domain and grid system were defined for the three geographic regions that were selected for simulation modeling. The modeling domain for each of the regions is presented in Figure 1. The Phoenix (PH) and Tucson (TC) domains are centered on the urbanized portion of Maricopa and Pima counties, respectively. These represent the two largest metropolitan areas of the state. The modeling domain for the Casa Grande (CG) was centered around the agricultural community of Pinal county. The selection of modeling domains

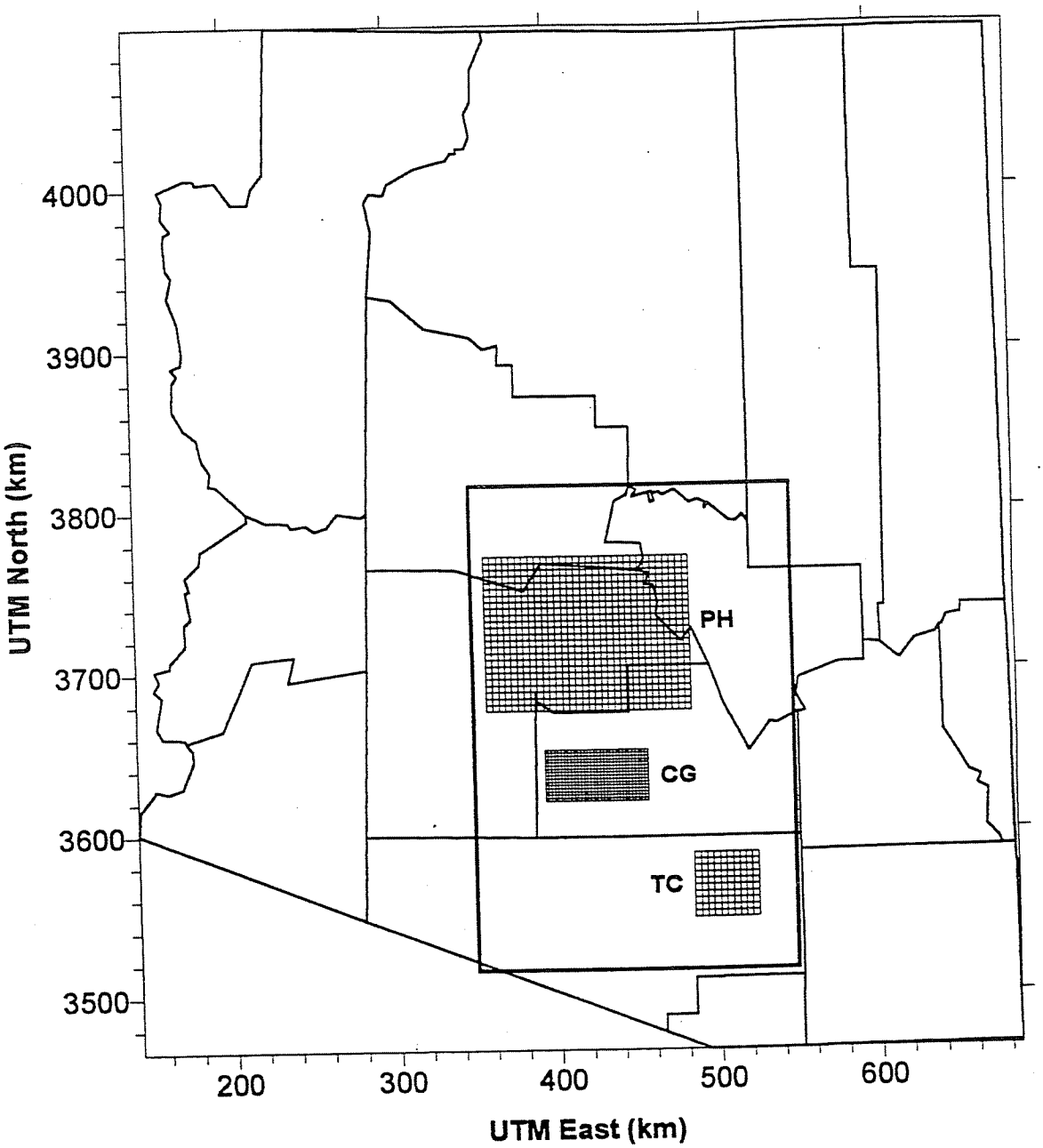

Figure 1 Modeling Domains and Grids

took into account the distribution of major emission sources, and the locations of the meteorological monitoring sites. Figure 1 also shows the emissions domain which encompasses the modeling domains. The emissions domain consists of 50 grid cells in the east-west direction and 75 grid cells in the north-south direction, with a horizontal grid spacing of 4 km. The 4 km grid spacing of the emissions domain allows us to better resolve the major emission sources. The grid systems, which define the horizontal resolution of the model, vary for the three regions, with finer resolution in smaller regions. Table 1 provides details of the grid system for each of the modeling domains. Six vertical layers will be used for the simulation. The surface (lowest) layer will be the shallowest with a thickness of 40 m and the upper layers will be progressively thicker, with the top of the modeling domain at 6 km.

TABLE 1

Definitions of the Atmospheric Modeling Domains

Domain	Southwest Corner (UTM E, UTM N km) (Zone 12)	Grid Cell Size (km)	Number of Grid Cells
Phoenix (PH)	357, 3675	4 × 4	32 × 24
Casa Grande (CG)	393, 3619	2 × 2	32 × 16
Tucson (TC)	485, 3547	4 × 4	10 × 10

Preparation of Meteorological Inputs for the Air Quality Model

The primary meteorological inputs for the air quality model consist of gridded fields of winds, temperature and relative humidity. These inputs are generated by a diagnostic meteorological model by interpolating observational data. The observational data used in the meteorological model consist of measurements of wind speed, wind direction, temperature, relative humidity and precipitation from the PRISMS, AZMET and the NWS networks. These data were obtained from Arizona State University, University of Arizona and the National Climatic Data Center (NCDC). Tables 2, 3 and 4 summarize the data obtained from the PRISMS, AZMET and the NWS networks, respectively. As seen in Figures 2, 3 and 4 the surface meteorological data obtained from the three networks are available for more that 50 monitoring sites but as seen in Figure 5, the upper-air data are limited to only four sites.

The generation of the meteorological input files for the air quality model involved (1)

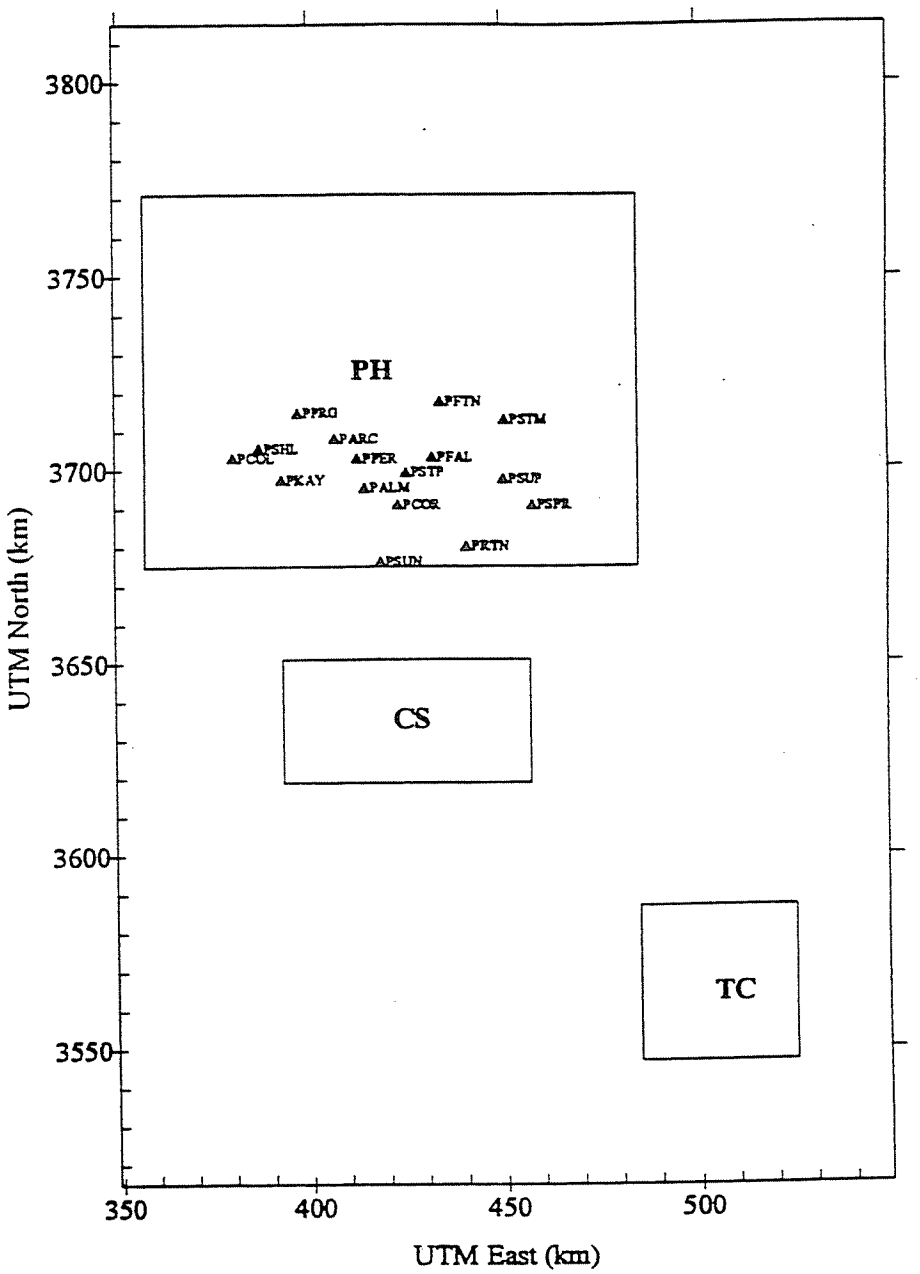

Figure 2. Surface wind monitoring sites from the PRISMS network

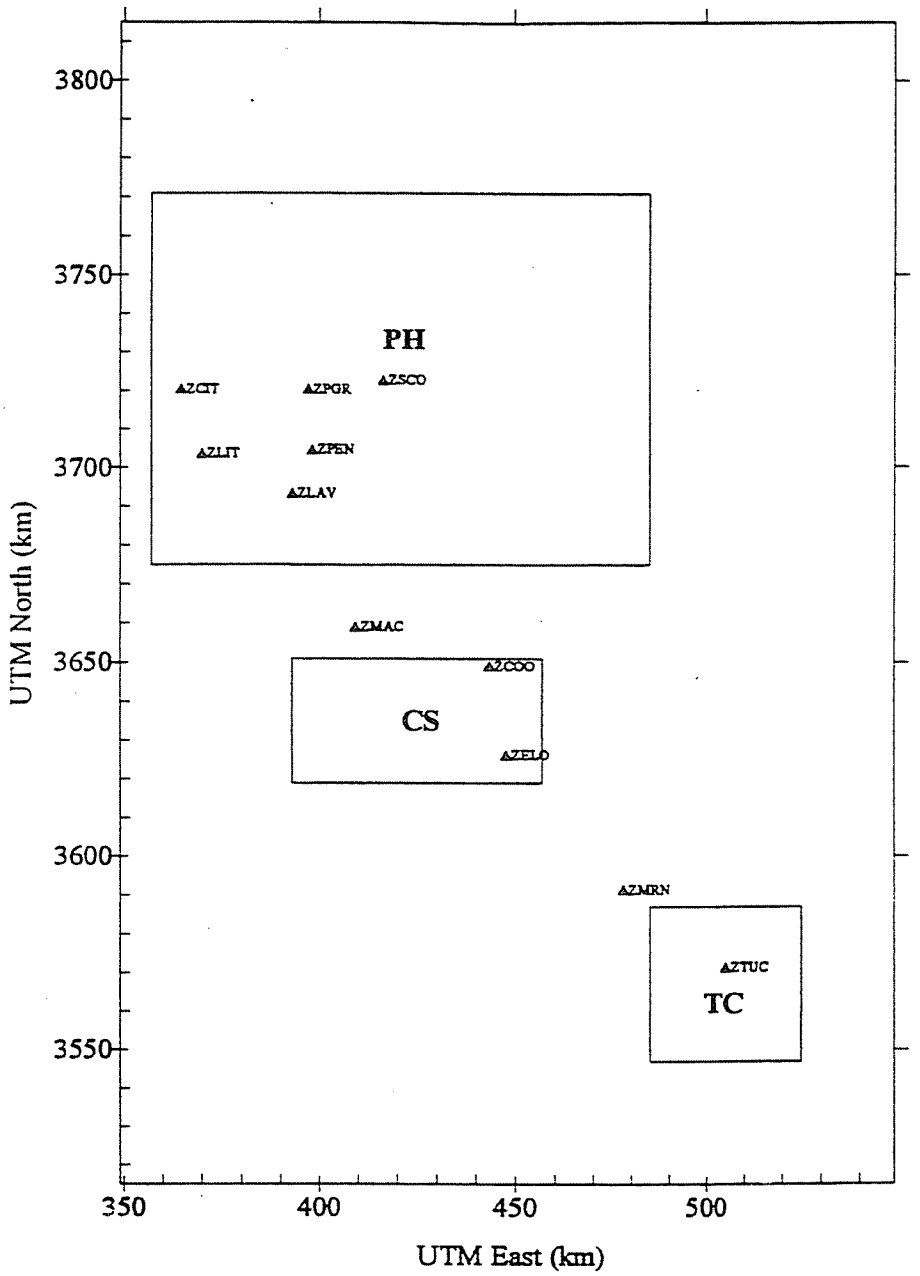

Figure 3. Surface wind monitoring sites from the AZMET network

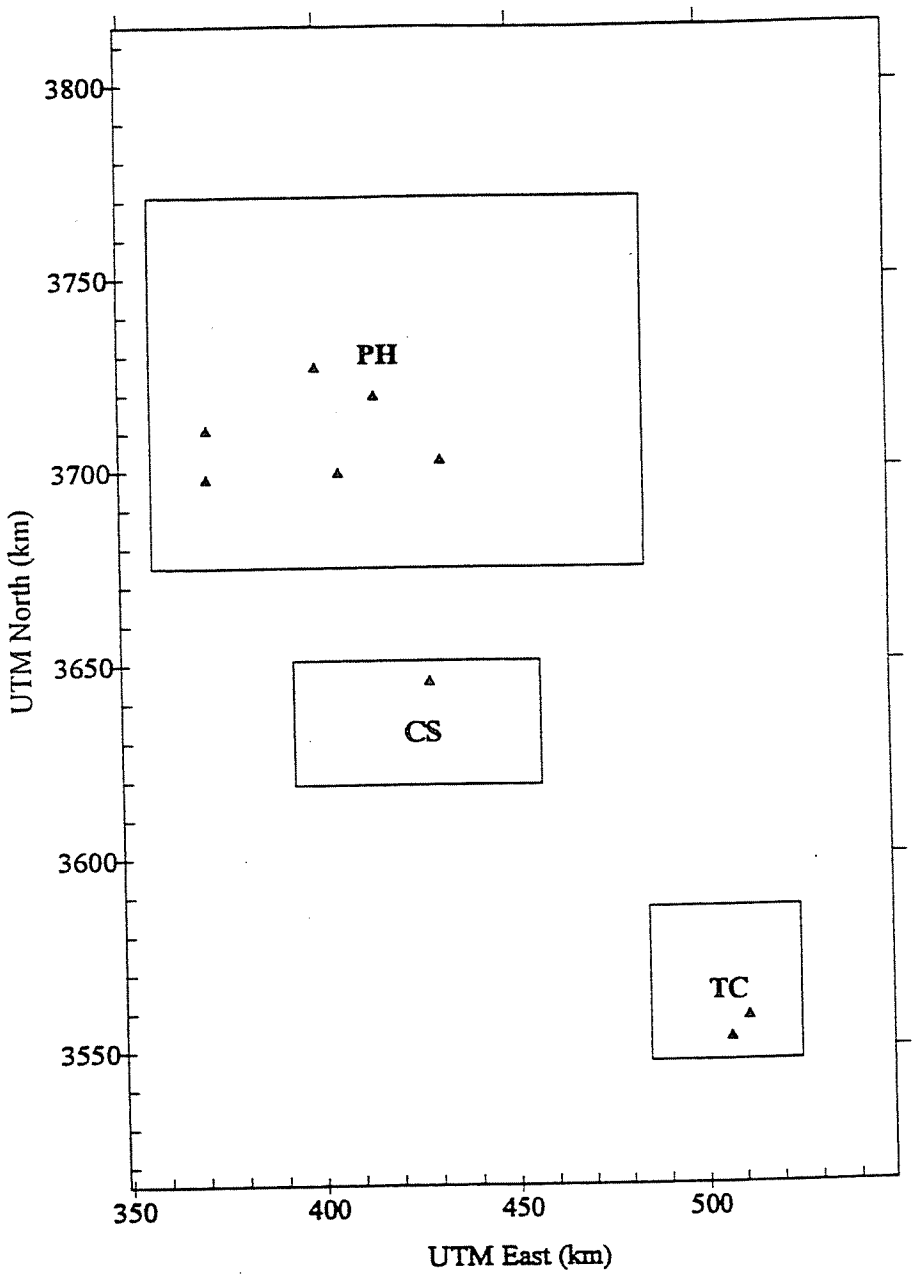

Figure 4. Surface wind monitoring sites from the NWS network

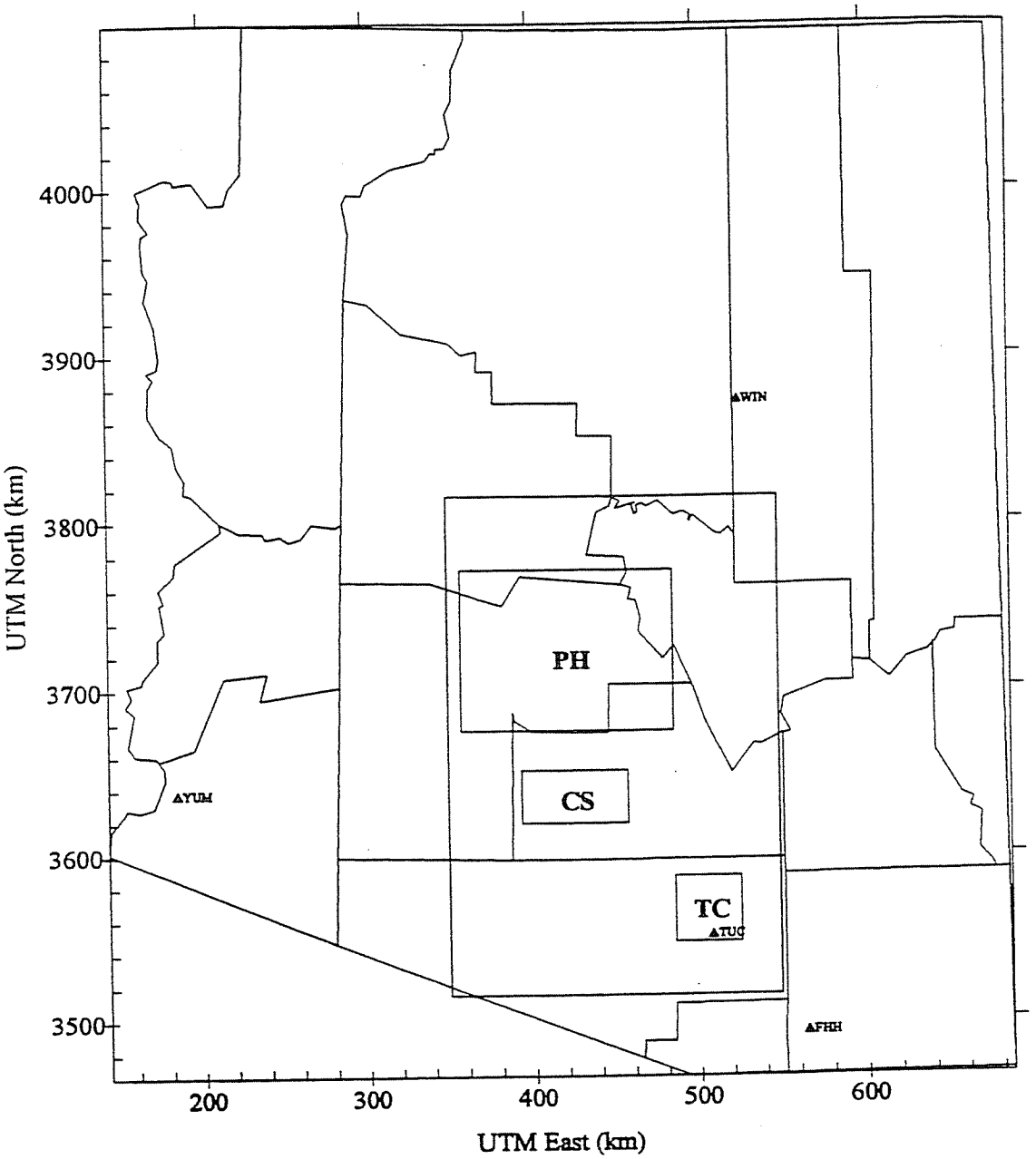

Figure 5. Upper-air wind monitoring sites from the NWS network

Table 2. Data availability from PRISMS network

Site ID	UTM East (km)	UTM North (km)	Elevation (m)
PALM	414.51	3695.41	359.67
PARC	406.85	3708.08	379.48
PCOL	380.17	3703.14	326.75
PCOR	422.94	3690.97	368.81
PFAL	431.96	3703.34	416.06
PFTN	434.19	3717.83	495.31
PKAY	392.83	3697.48	313.95
PPER	412.77	3702.94	384.05
PPRG	397.20	3714.89	374.91
PRTN	440.64	3680.16	429.77
PSHL	386.98	3705.64	326.14
PSTP	425.23	3699.42	365.76
PSTM	450.49	3713.12	438.92
PSUN	418.53	3676.31	365.76
PSUP	450.09	3697.63	533.41
PSPR	457.63	3690.91	548.65

Table 3. Data availability from AZMET network

Site ID	UTM East (km)	UTM North (km)	Elevation (m)
ZTUC	505.10	3571.30	713.24
ZCOO	443.49	3649.03	422.15
ZMAC	409.29	3659.11	361.19
ZCIT	364.58	3720.57	406.91
ZLIT	370.07	3703.76	309.07
ZPGR	397.18	3720.53	400.82
ZMRN	478.07	3591.37	601.38
ZPEN	398.12	3704.75	335.28
ZELO	447.84	3626.16	461.17
ZSCO	416.53	3722.75	469.40
ZLAV	393.02	3693.41	316.08

Table 4. Data availability from the NWS network

Site ID	Site Name	UTM North (km)	UTM East (km)	Elevation (m)
722740	Tucson Intl. Airport	506.29	3553.17	779.00
722745	Davis-Monthan AFB	511.00	3558.72	824.00
722748	Casa Granda (AWOS)	428.33	3645.80	446.00
722780	Phoenix/Sky Harbor	405.48	3699.59	337.00
722783	Mesa/Falcon Field	431.85	3703.07	424.00
722784	Deer Valley/Phoenix	399.58	3727.37	450.00
722785	Luke AFB/Phoenix	371.54	3711.07	332.00
722788	Goodyear Municipal	371.37	3698.14	295.00
722789	Scottsdale Municipal	414.95	3719.84	460.00
723745	Payson	469.30	3787.88	1498.00
TUC	Tucson*	507.55	3551.32	802.00
WIN	Winslow*	525.55	3872.89	1487.00
FHH	Fort Huachuca*	564.54	3492.77	1428.00
YUM	Yuma*	183.60	3637.29	98.00

* Upper Air Stations

preprocessing of the observed meteorological data for input to the meteorological model, (2) specification of the meteorological model input parameters, (3) simulation of the meteorological model for the 1994 simulation year, and (4) quality assurance of the meteorological inputs of the air quality model.

Preprocessing the observational data was required since data from individual networks were available in different consistency and formats. These data sets were processed individually and reformatted in consistent formats as required by the meteorological model. In some cases, the surface data was temporally interpolated to provide hourly inputs to the meteorological model.

The meteorological model generates hourly, gridded, horizontal wind fields and vertical velocity fields for each layer of the air quality model. The gridded meteorological data were plotted and examined to ensure accurate representation of the observed data, temporal and spatial consistency and reasonableness. Vector plots of gridded wind fields were plotted at the surface and the vertical model layers. Vectors representing the wind observations were overlaid on the gridded wind fields to facilitate comparison between the calculated and observed wind fields.

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APPENDIX F

Toxicity and Exposure Assessment and Risk Characterization

TOXICITY AND EXPOSURE ASSESSMENT AND RISK CHARACTERIZATION

1. TOXICITY ASSESSMENT

The purpose of the toxicity assessment is to identify the types of adverse health effects COI may potentially cause, and to define the relationship between the dose of a COI and the likelihood or magnitude of an adverse effect (response). Adverse effects are characterized as carcinogenic or "noncarcinogenic" (i.e., potential effects other than cancer). Numerical dose-response relationships are defined by U.S. EPA for oral exposure and for exposure by inhalation. Oral dose-response values are also used for dermal exposures because values have not yet developed for this route of exposure. Combining the results of the dose-response assessment with information on the magnitude of potential human exposure provides an estimate of potential risk.

Sources of the published dose-response values that are being used in the Risk Assessment include U.S. EPA's Integrated Risk Information System (IRIS) (U.S. EPA, 1993a), the Health Effects Assessment Summary Tables (HEAST) (U.S. EPA, 1993b) and values provided by the U.S. EPA Environmental Criteria and Assessment Office (ECAO) in Cincinnati, Ohio, and, for chemicals that do not have U.S. EPA-derived values, the California Environmental Protection Agency (CalEPA) (CalEPA, 1994). These values are discussed below.

1.1 Carcinogenic Dose Response

Data on the chemical causes of cancer in humans is limited. It is usually inferred from experiments with laboratory animals. The human carcinogenic potential of a chemical is classified based on the weight of the scientific evidence. Accordingly, the U.S. EPA classifies chemicals into one of the following groups:

- Group A: Human Carcinogen (sufficient evidence of carcinogenicity in humans)
- Group B: Probable Human Carcinogen (B1 = limited evidence of carcinogenicity in humans; B2 = sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans)
- Group C: Possible Human Carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data)

- Group D: Not Classifiable as to Human Carcinogenicity (inadequate or no evidence)

- Group E: Evidence of Noncarcinogenicity for Humans (no evidence of carcinogenicity in adequate studies)

Cancer potency information is provided as a cancer slope factor (CSF) or as a unit risk estimate (URE). CSFs are expressed in terms of $(mg/kg\text{-}day)^{-1}$ [or kg-day/mg]. When multiplied by a lifetime average daily dose expressed in terms of mg/kg-day, the product is unitless and represents the risk of contracting cancer, over and above the background cancer rate. Unit risk values for inhalation exposures are expressed in units of $(\mu g/m^3)^{-1}$ [or $m^3/\mu g$], and represent the probability of a person contracting cancer as a result of continuous exposure to an ambient concentration of a chemical of 1 $\mu g/m^3$ over a 70 year lifetime. Multiplying the URE by an air concentration expressed in terms of $\mu g/m^3$ provides an estimate of the risk of contracting cancer as a result of the exposure to that concentration of the chemical over a lifetime.

The underlying assumption of regulatory risk characterization for compounds with known or assumed potential carcinogenic effects is that no threshold dose exists. Thus, the characterization assumes that there is some finite level of risk associated with each dose, no matter how small. Computerized models have been developed that extrapolate dose-response relations observed at the relatively high doses used in animal studies to the low dose levels encountered by humans in environmental situations.

Cancer Slope Factor. In deriving CSFs, the U.S. EPA and other regulatory agencies incorporate both the no-threshold assumption and a further assumption that carcinogenic dose-response is linear at low doses. The mathematical models used to extrapolate animal data to humans are statistical models that yield a distribution of cancer potency estimates. Because a great deal of uncertainty is associated with potency estimation, regulatory agencies make assumptions in order maximize the protection of health. Thus, data from the most sensitive species are used to develop the CSF, and data from the tumor sites that show the most significant increase in tumor incidence are used, whether or not significant lower potency is observed at other sites or in other species. Another such health-protective assumption is the use of the "upper-bound" estimate of the cancer potency in deriving CSFs to avoid the possibility of underestimating the risk to humans.

Finally, it is assumed that potency scales between species on a surface area basis, which is estimated by body weight to the 2/3 power ($BW^{2/3}$). The U.S. EPA has recently proposed that scaling by $BW^{3/4}$ is more appropriate (57FR24152, June 5, 1992), but this change has not yet been implemented. Scaling by either factor concludes that humans are more sensitive to the

toxic effects of chemicals than the laboratory species in the bioassay used to develop the dose-response value.

Unit Risk Estimate. Dose-response values for the inhalation route of exposure are provided by the U.S. EPA as Unit Risk Estimates (URE). In order to use these dose-response values to calculate an average daily exposure dose, the UREs are converted to CSFs. The conversion from URE to CSF follows the formula cited in HEAST (U.S. EPA, 1993b):

$$\text{URE } (m^3/\mu g) \times (70 \text{ kg}) \times (\text{day}/20\ m^3) \times (\text{mg}/1000\ \mu g) = \text{CSF (kg-day/mg)}$$

1.2 Noncarcinogenic Dose-Response

Compounds with known or potential noncarcinogenic effects are assumed to have a dose below which no adverse effect occurs or, conversely, above which an adverse effect may be seen. This dose is called the threshold dose. An estimate of the threshold dose that is based on experimental determination that no effect occurs at a given dose is called a No Observed Adverse Effect Level (NOAEL). The true threshold can be assumed to be at or above the NOAEL. The lowest dose at which an adverse effect has been observed in an experiment is called a Lowest Observed Adverse Effect Level (LOAEL). The true threshold dose is somewhere below the LOAEL. The type of adverse effect, such as liver damage, change in kidney function, altered respiratory function, or a change in a blood parameter, with which the NOAEL or LOAEL is associated, is termed the critical effect for the study.

By applying uncertainty factors to the NOAEL or the LOAEL, References Doses (RfDs) and Reference Concentrations (RfCs) for chronic exposures to chemicals with noncarcinogenic effects have been developed by the U.S. EPA (1994a, 1994b). Uncertainty factors are applied to the NOAEL or LOAEL to account for uncertainties associated with the dose-response relationship due to using an animal study to derive a human dose-response value, extrapolating from short term studies to long term exposures, and to reflect effects on sensitive subpopulations. Generally, a 10-fold factor is used to account for each of these uncertainties; thus, the total uncertainty factor can range from 10 to 10,000.

This use of uncertainty factors assumes that humans are more sensitive to the toxic effects of chemicals than animals, and therefore, the estimated human threshold can be several orders of magnitude below the threshold defined in an animal study. For compounds with noncarcinogenic effects, an RfD or RfC that is thus derived provides reasonable certainty that noncarcinogenic health effects are not expected to occur even if daily exposures were to occur at the RfD or RfC for a lifetime.

RfDs (and exposure doses) are expressed in units of milligrams of chemical per kilogram of body weight per day (mg/kg-day). RfCs are dose-response values specifically for the inhalation route of exposure and are expressed as milligrams of compound per cubic meter of air (mg/m^3). In order to use these dose-response values to calculate an average daily exposure dose, the RfCs are converted to RfDs for a 70 kg (about 155 lb) body weight and assuming that 20 m^3 of air is inhaled during one day. Thus the conversion from RfC to RfD follows the formula cited in HEAST (U.S. EPA, 1993b):

$$RfC\ (mg/m^3) \times (1/70\ kg) \times (20\ m^3/day) = RfD\ (mg/kg\text{-}day).$$

In accordance with U.S. EPA ECAO policy, the evaluation of noncarcinogenic effects following inhalation exposures is being made only for those chemicals whose toxic effects have been studied following inhalation exposures, and for which U.S. EPA has developed RfC values.

1.3 Acute Dose-Response

Acute health effects can be important when considering inhalation exposures. Acute dose-response information is not readily available from the U.S. EPA. However, the CalEPA has recently developed acute dose-response values for a variety of chemicals, and these are being used in the Arizona HAPs risk assessment. For COI in the risk assessment that do not have acute dose-response values, the Threshold Limit Values (TLVs) developed by the American Congress of Governmental Industrial Hygienists (ACGIH) for workplace inhalation exposures to chemicals are being evaluated, in consultation with ADHS personnel, as to their applicability for assessing acute health effects in the general population.

2. EXPOSURE ASSESSMENT

The exposure assessment estimates the amounts of COI to which humans are exposed over various periods of time. It consists of several components that lead to the calculation of an average daily dose (ADD) for chronic exposures, expressed as mass of substance per unit body weight per day (mg/kg-day) for each COI by each pathway. Development of the exposure assessment requires the following steps:

1. Receptor identification,
2. Identification of exposure pathways,
3. Definition of exposure calculation equations
4. Definition of receptor-specific exposure parameters, and
5. Definition of chemical-specific exposure parameters.

Each of these is discussed in turn below.

foodstuffs. Produce grown in backyard gardens or commercially may take up COI from the soil, or COI may directly deposit onto the surface of the produce. A subset of COI may be expected to bioaccumulate in animal products. If beef or dairy farms occur within the region of interest, certain COI may concentrate in the meat and milk. These pathways include the evaluation of livestock exposure to COI via soil ingestion, drinking water ingestion, and crop ingestion.

Thus, for the multimedia pathway analysis for Phoenix, concentrations of COI in crops are being calculated to take into account HAPs contributions from deposition and uptake from the soil. Should the analysis indicate that beef and dairy pathways are appropriate for evaluation, we will also perform an analysis of human exposure to COI via consumption of mothers' milk. The COI evaluated in the beef, dairy and mothers' milk pathways will be selected based on the availability of chemical-specific biotransfer factors, or on the availability of data to develop such factors.

2.3 Dose Calculation

Exposure to COI from inhalation, in terms of an average daily dose (ADD), is being estimated as follows:

ADD (mg/kg-day) = Concentration in air (mg/m^3)
x Inhalation rate (m^3/day)
x Inhalation absorption adjustment factor (unitless)
x Exposure time per day (hr/24 hours)
x Days exposed per year (day/365 days)
x Exposure duration (years)
÷ Body weight (kg)
÷ Averaging period (years).

This formula is designed for chronic exposures, but the same approach is used for estimating acute exposure dosages. The terms in this formula are discussed below. Receptor-specific exposure parameters are discussed first, followed by a the chemical specific exposure parameters.

2.4 Receptor Specific Parameters

Receptor-specific exposure parameters describe the attributes of the receptor as well as the receptor-media interactions. Many state and federal guidance documents provide highly-protective default values for these parameters, but these defaults are intended for use in regulatory risk assessment. In order to tailor the evaluation for the State of Arizona, as well as for the regions to be evaluated, region-specific data have been obtained from the scientific literature and from contact with officials from both state and local governments.

Using this information, parameters have been developed, in conjunction with ADEQ and ADHS personnel, for each receptor (RME and CTC), and for each age group (young child, older child, and adult) for the inhalation exposure pathway for each region. These parameters are discussed below. Corresponding parameters for the multimedia exposure assessment are still being finalized.

Exposure Time. As noted above, exposure is being evaluated on a regional basis. It is assumed that all receptors are exposed to COI in ambient, outdoor, air via inhalation 24 hours per day while in the region. No distinction is made between outdoor and indoor air exposures. While some estimates suggest that indoor air concentrations of outdoor HAPs may be some fraction of outdoor concentrations, this does not account for HAP emissions within the home. An evaluation of indoor air exposures is currently being undertaken by the ADHS; however, results are not available for inclusion in this analysis. Therefore, a 24 hour per day exposure time is assumed for all receptors.

Exposure Duration. Most risk assessment guidance has been designed to evaluate localized exposures to chemicals associated with a single site or emissions source. The U.S. EPA has calculated average and upper-bound residential occupancy periods of 9 and 30 years for residency in a single house (U.S. EPA, 1989).

Since the Arizona HAPs research program is evaluating exposure to HAPs on a regional basis, an estimate of a residential occupancy period within a region (a regional occupancy period) is a more appropriate estimator of exposure to HAPs than a residential occupancy period within a single house. It would be expected that the regional values would be greater than the household values, because people can move from house to house, or apartment to apartment, and still remain within the same region.

In order to estimate a regional occupancy period, a model entitled "ROPSIM" developed by the U.S. EPA was employed (U.S. EPA, 1992a). The model predicts the occupancy period of a U.S. resident within a single residence using census data for time spent in the current residence by year of age as well as mortality data for each year of age.

Although the model is available from the EPA, it is only available in a form for use on a mainframe computer. ENSR has developed a PC-based version of the model, and has validated it by reconstructing the results presented by the authors of the EPA model for single residence occupancy periods. The model uses U.S. census data on the number of years spent in the current residence to calculate the per-residence values. ENSR used the same census data, but used as input to the model the number of years spent in the current county. For the HAPs evaluation, it is assumed that the per-county value is predictive of a per-region value. Use of the county values also assumes that the use of U.S. data is appropriate for the regions in Arizona.

Unfortunately, residency period census data was not available on a county or state-wide basis for Arizona.

The model calculates that the average continuous duration of residence within a single county in the U.S. is 21 years, and the upper-bound (95th percentile) value is 59 years. Therefore, an exposure duration of 21 years is being used to evaluate the CTC receptor. This receptor is evaluated for 6 years as a young child (aged 0-6 years), 12 years as an older child (aged 6-18 years), and 3 years as an adult (aged 18-21 years). An additional CTC receptor is being evaluated as an adult for a 21-year duration of exposure. Similarly, exposure durations of 59 years, from birth to age 59 and also from age 18 to age 77, are being used to evaluate the RME receptor.

Days Exposed per Year. In order to provide an upper-bound estimate of exposure for the RME case, we have assumed that this receptor is exposed to air in the region for 365 days per year. For the CTC receptor, we have assumed that 2 weeks are spent outside of the region for vacation, etc. Therefore, the CTC receptor is assumed to be exposed to regional HAPs 350 days per year.

Averaging Period. The calculation of the ADD is slightly different for cancer and noncancer evaluations. For noncancer assessments, exposures are assumed to have a potential for eliciting adverse effects only during the period of exposure. Therefore, the averaging time for a noncancer assessment is the duration of exposure, and the ADD is referred to as a Chronic Average Daily Dose or CADD. The averaging periods equal the durations of exposure, which are 59 years for the RME receptor and 21 years for the CTC receptor.

For the evaluation of potential carcinogenic effects, the risk of contracting cancer within a person's lifetime is calculated based on the Lifetime Average Daily Dose (LADD). The averaging period for the LADD is the lifetime of the receptor. For these purposes, the average lifetime of a U.S. resident, of 70 years, is used for both receptors (U.S. EPA, 1989).

Body Weight. The risk assessment for both receptors uses the average body weight for each age group, as calculated from U.S. EPA (1985) data on body weights by age for U.S. residents. The average weight for males of each age was averaged for each age group. Therefore, the average body weight for the young child aged 0-6 years is 14 kg (31 lbs), and for the older child aged 6-18 years is 42 kg (92 lbs). The average adult body weight for U.S. residents of 70 kg (155 lbs) was used for each adult receptor (U.S. EPA, 1989).

Inhalation Rate. Two methods are available for estimating daily inhalation rates: one is based on level of activity patterns for various age groups, and the other is based on basal metabolic rate. Because the receptors in this assessment are being evaluated for daily exposure to HAPs

over a period of many years, rather than for exposures during defined periods of activity, inhalation rates based on basal metabolic rate are employed. The age group values have been selected from distributions presented by Finley et al. (1994), based on the basal metabolic rate models of Layton (1993).

For the RME receptor, the average 95th percentile inhalation rate data for each age group is used in the risk assessment. These values are 9.3 m^3/day for the young child aged 0-6 years, 16.8 m^3/day for the older child aged 6-18 years, and 18 m^3/day for an adult aged 18-59 years. A value of 17.6 m^3/day is used for the RME adult receptor aged 18-77 years.

For the CTC receptor, the average 50th percentile inhalation rate data for each age group is used in the risk assessment. These values are 6.6 m^3/day for the young child aged 0-6 years, 11.5 m^3/day for the older child aged 6-18 years, and 14.8 m^3/day for an adult aged 18-21 years. A value of 13.5 m^3/day is used for the RME adult receptor, aged 18-39 years.

2.5 Chemical-Specific Exposure Parameters

Chemical-specific exposure parameters are required for each of the exposure pathways. For the inhalation pathway, air concentration data are required. These air concentrations vary over time and over the geographical area. People themselves are mobile to varying degrees. Some live in one area, shop in another area, and work or attend school in a third. Others, such as the elderly, may spend all of their time in one relatively small area, and yet others, such as sales persons or delivery workers, may travel extensively within a region. Because both the RME and CTC receptors are intended to evaluate typical exposures within each region, and because it is assumed that people move around within a region, the air concentrations predicted by the model are being averaged over the populated areas in each region and over the period of a year to evaluate exposures for both classes of receptors.

Absorption adjustment factors (AAFs) are also necessary for some exposure evaluations. AAFs are used to ensure that the calculated human exposure dose is expressed in the same terms as the doses used in the calculation of the dose-response values, and that differences in absorption of a chemical between animals and humans and between exposure routes are accounted for. For example, most risk assessment calculations estimate a human exposure dose, but the dose-response value may be expressed in terms of an absorbed dose in animals; or, an oral study in animals may have been used to estimate an inhalation dose-response value for humans.

Other chemical-specific exposure parameters associated with a multipathway assessment include: skin permeability constants required for the evaluation of dermal contact with COI in water (U.S. EPA, 1992b); root uptake factors required for the estimation of produce and crop

concentrations of COI; and biotransfer factors required to predict meat and milk concentrations of COI in livestock; and similarly, biotransfer factors and tissue half-life estimates required for the calculation of concentrations in mother's milk.

3. RISK CHARACTERIZATION

Risk characterization is the step in the risk assessment process that combines the results of the exposure assessment and the dose-response assessment for each compound of interest in order to estimate the potential for carcinogenic and noncarcinogenic human health risks from chronic and acute exposure to that compound.

Characterization of the potential impact of carcinogenic and non-carcinogenic compounds are approached in very different ways. The difference in approaches derives from the health-protective assumption that compounds with possible carcinogenic action proceed by a no-threshold mechanism, whereas compounds that exhibit no carcinogenic effects may have a threshold, a dose below which few individuals would be expected to respond. Thus, under the no-threshold assumption, it is necessary to calculate a risk, while for compounds with a threshold, it is possible to simply characterize an exposure as above or below a Reference Dose. This section summarizes how the noncarcinogenic and carcinogenic risks are characterized in the Arizona HAPs assessment.

3.1 Carcinogenic Risk Characterization

The carcinogenic risk characterization estimates the upper bound likelihood, over and above the background cancer rate, that a receptor will develop cancer in his or her lifetime as a result of exposures to the HAPs evaluated as COI. Cancer slope factors for compounds with potential carcinogenic effects are multiplied by the estimated lifetime average daily doses (LADD) to estimate this risk. The LADD is used in the calculation of cancer risk because exposure and cancer risk are relevant to the lifetime of the individual. The probability of cancer occurrence associated with a certain level of exposure is estimated by the following relationship:

$$\text{Excess Lifetime Cancer Risk} = 1 - \exp(-\text{CSF} \times \text{LADD})$$

The LADD is expressed as milligrams of compound per kilogram of body weight per day (mg/kg-day) averaged over a 70 year lifetime. CSFs are correspondingly expressed in units of (kg-day/mg). Thus, the product of exposure and potency is unitless.

When the potency-exposure product, CSF x LADD, is much greater than one, the Excess Lifetime Cancer Rate (ELCR) approaches one (i.e., 100% probability). When the product is less than about 0.01, the equation simplifies to the approximate form:

ELCR = CSF x LADD

The product of the CSF and the LADD is unitless and provides an upper bound estimate of the potential carcinogenic risk associated with a receptor's exposure to that compound via that pathway. ELCRs are being calculated for each potentially carcinogenic COI.

Carcinogenic risks are assumed to be additive. Therefore, for each receptor, the ELCRs for each pathway by which the receptor is assumed to be exposed are calculated by summing the potential risks derived for each compound. A total ELCR is then calculated by summing the pathway-specific ELCRs.

In order to indicate the implications of the ELCRs to the total population in each study region, the number of excess cases of cancer that might occur in the entire population there during a year will be estimated. This estimate is made by multiplying the ELCR by the population and dividing the result by the exposure duration in years.

3.2 Noncarcinogenic Risk Characterization

The potential for exposures to COI that result in adverse noncarcinogenic health effects is estimated for each receptor by comparing the Chronic Average Daily Dose (CADD) for each compound (derived as described in the Section 2.4) with the Reference Dose for that compound (discussed in Section 1.2). The resulting ratio, which is unitless, is known as the Hazard Quotient (HQ) for that compound. The HQ is calculated using the following formula:

Hazard Quotient = CADD (mg/kg-day) / RfD (mg/kg-day).

As an initial screen, the HQs for each COI that the receptor is assumed to be exposed to via a specific pathway are summed to yield the Hazard Index (HI) for that pathway, and a total HI is then calculated for each receptor by summing the pathway-specific HIs. A total HI of less than 1 for a given receptor indicates that no adverse noncarcinogenic health effects are expected to occur as a result of that receptor's potential exposure to COI.

As mentioned above, toxic effects other than cancer are assumed to exhibit a threshold. In noncarcinogenic risk assessment, the toxic or critical effects of interest are diverse. For example, the magnitude of a toxic effect from exposure to a chemical that is a kidney toxin is not necessarily increased when exposure to a liver toxin occurs simultaneously. However, it is recognized that exposure to two chemicals that act on the liver may have combined effects.

The current state of risk assessment does not take into account synergism or antagonism between chemical effects. Although there are ongoing efforts to understand these processes,

current knowledge does not allow for a quantitative evaluation of these effects. Therefore, as an approximation, HQs are often summed for chemicals that have similar toxic endpoints, as defined in the derivation of the RfD or RfC. Such an evaluation is termed a toxic endpoint-specific analysis. If the HI is below 1.0, no adverse effects are expected to occur with respect to that specific endpoint. Such a refined analysis is not considered necessary unless the total receptor HI exceeds 1.0.

3.3 Acute Risk Characterization

The risk assessment for acute inhalation effects is being conducted in much the same manner as described above for the chronic noncarcinogenic evaluation. However, both the exposure and dose-response values are expressed in terms of air concentrations, rather than a daily exposure dose. A toxic endpoint analysis is performed as necessary.

3.4 Uncertainty Analysis

There are many uncertainties in the risk assessment process, and in order to make informed decisions based on risk assessment results, it is necessary to understand not only the magnitude of the risk, but what assumptions are likely to affect that outcome. An uncertainty analysis is being performed to evaluate each step of the risk assessment process, including the emissions characterization and the atmospheric model, identify where assumptions had to be made and estimate whether the assumptions used are likely to result in an over-estimation or an under-estimation of health risks.

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